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EFFECTS OF CHEMICAL DISSOCIATION AND MOLECULAR

VIBRATIONS ON STEADY ONE-DIMENSIONAL FLOW

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SUMMARY

Equations are derived from which the one-dimensional flow of gases simultaneously subject to dissociation and vibration can be computed. The cases considered include both frozen and equilibrium flows and flows where either dissociation or vibration is frozen while the other is in equilibrium. These flows are isentropic if no shocks occur in the region considered and if viscosity and heat conduction are negligible.

It is found that for flow of the gas in chemical equilibrium the temperature and the degree of dissociation are convenient independent variables to use. They are related through the entropy, a constant along the flow.

Flows in which the chemical reaction and vibrations are not in equilibrium are also studied. In these flows the entropy increases along the streamtubes, even when viscosity, heat conduction, and shock waves are absent. The analysis of nonequilibrium flow is much simplified by the introduction of a vibrational temperature. Further, the definition of entropy is generalized to include the case of the reacting vibrating gas out of equilibrium. Nonequilibrium flow cannot be treated with the same generality as isentropic flow, because some specific mathematical constraint is required to fully specify the flow. Some of the rather specific results which come from the examples treated are:

(1) In the relaxation region behind a shock wave in a shock tube, pressure and density are related by a simple formula, which is not of the polytrope form.

(2) If the relaxing flow behind a normal shock is at constant density, or at constant pressure, then the streamtube contracts. The contraction for constant density flow is the larger, the higher the free-stream Mach number; for constant pressure the total area change is about a factor of 2/7 when only vibrations relax.

(3) Relaxing isothermal flow behind a normal shock corresponds to a rapidly expanding streamtube.

(4) If in a shock tube both vibrational relaxation and chemical reaction are occurring behind the normal shock wave, then both the degree of dissociation and the degree of vibrational excitation can be calculated from measurements of the pressure and temperature distributions behind the wave.

When vibration and dissociation are both occurring simultaneously, then the two processes can, in general, be expected to interact. The coupling can be included in a simple approximate model of the relaxation. When the reaction is relatively very fast, this model of the relaxation process yields the result that the density overshoots its equilibrium value, then decreases to below its equilibrium value and finally reaches equilibrium from below. A bibliography is given at the end of the report.

INTRODUCTION

Until a few years ago, in the solutions to problems of supersonic aerodynamics, the assumption was usually made that the air was an inert gas, and that the ratio of specific heats was a constant. More recently some of these problems have been solved again, allowing for certain chemical reactions as well as the excitation of molecular vibrations. In this case it has usually been assumed that the air is in thermodynamic equilibrium everywhere in the flow field (e.g., refs. 1 through 5).

The temperature at the downstream side of the shock wave which is formed by a body moving through a gas at high Mach numbers is high enough to induce chemical reactions and excitation of molecular vibrations. If these processes occur very slowly, the reactions and molecular vibrations may be regarded as "frozen," and the constant γ solution is applicable. On the other hand, if these reactions and excitations occur very rapidly, then the thermodynamic equilibrium solution is valid.

A third case which may arise is that a particular reaction is neither sufficiently fast to be regarded as frozen nor sufficiently slow to be regarded as in chemical equilibrium. This occurs when the time characteristic of the reaction is comparable to the ratio of the characteristic length of the problem to the flow velocity. In this case the flow will under no circumstance be isentropic because the finite reaction rate introduces an entropy increase. In general, the flow will have some features qualitatively different from those of equilibrium flow or frozen flow. The flow problems with finite chemical reaction rates or finite rates of excitation of the molecular vibrations are considerably more difficult than the frozen flow problems or equilibrium problem.

The present paper is devoted to developing a general method by which one is able to deal with frozen and equilibrium flow as well as non-equilibrium flow for simple situations. The central idea is to introduce the vibrational energy and the degree of dissociation as two additional (in general, independent) variables. If the process measured by either

one of these variables is frozen or in equilibrium, then the formal statement of this fact allows one to eliminate this variable from the equations.

The paper falls into three parts: (1) The conservation equations are set up for the general case, using vibrational energy and degree of dissociation as variables. The equation for the entropy change of relaxing flow is also given. (2) The isentropic flows are found and the solutions for the one-dimensional flow in the isentropic cases are given. In particular, simple relationships that exist between pairs of variables, such as pressure and temperature, are derived. The results for the frozen and equilibrium flows (both of which are isentropic) are exhibited explicitly whenever possible, permitting ready comparison. (3) Flows with finite relaxation lengths are analyzed. In this case, since there exist one or two additional independent variables, it is required that some further restriction be put on the flow before a unique solution can be obtained. Invariably a length, characterizing the relaxation process, enters into the problem and the absolute dimensions of the streamtube become important. In this respect, the results are qualitatively different from those for isentropic flow; still the nonisentropic solutions reduce to the appropriate isentropic ones if the relaxation lengths are extremely long or extremely short compared to the geometric parameters in the problem. Some specific and rather simple cases will be analyzed in detail. In particular, the coupled relaxation of vibrations and reaction is worked out for flow in a shock tube.

There are several papers on the nonequilibrium features of flow. Those by Freeman (ref. 6) and by Bray (ref. 7) treat relaxation due to dissociation in the "idealized gas" introduced by Lighthill (ref. 5), but do not include vibrational relaxation. Detailed analyses of the relaxation due to oxygen dissociation have been made by Wood (ref. 8) and Evans (ref. 9), and oxygen recombination in air has been analyzed by the present author (ref. 10). There, too, the vibrational heat capacity lag is neglected. References to earlier work are given in reference 10. Rather general formulas which apply to nonisentropic flow are given by Resler in reference 11 and also by Wood and Kirkwood (ref. 12). A numerical integration of flow across a shock including not only relaxation of internal degrees of freedom but also viscosity and heat conduction has been carried through by Talbot (ref. 13).

The position of the present paper is intermediate between those which contain detailed numerical integration using tabulated thermodynamic functions for air and those which make use of the simple Lighthill gas model. It is an attempt to strike a happy medium between accuracy and simplicity as well as between generality and explicitness. Although the chemistry and thermodynamics discussed here are of general applicability, attention is restricted to one-dimensional flow where the solutions can be given in explicit algebraic form.

SYMBOLS

a	the variation of $\sqrt{\dfrac{dp}{d\rho}}$ taken along streamlines; sound speed
A	cross-sectional area
A_2	any homonuclear diatomic molecule
B	number of atoms, in free or combined form, per unit mass of fluid
C	constant density characteristic of a particular gas A_2 (Numerical values are given in appendix B.)
C_p, C_ρ	dimensionless specific heats, $\left.\dfrac{\partial h}{\partial T}\right)_p$, $\left.\dfrac{\partial e}{\partial T}\right)_\rho$
D	dissociation energy per diatomic molecule
e	internal energy per unit mass divided by $\dfrac{N_O D}{M_{A_2}}$
f	partition functions
h	enthalpy per unit mass divided by $\dfrac{N_O D}{M_{A_2}}$; also Planck's constant
k	Boltzmann's constant
$K = K(T)$	equilibrium constant, defined in equation (20)
$K'(T, T_v)$	equilibrium constant with frozen vibrations, defined in equation (21)
m	mass flux per unit cross section in units of density, p'u
M	molecular weight
n	number of molecules per unit volume
N, N_2	nitrogen
N_O	Avogadro's number
$0, 0_2$	oxygen

p' pressure

p pressure divided by $m\left(\dfrac{N_0 D}{M_{A_2}}\right)$

R universal gas constant

S entropy per unit mass, divided by $\dfrac{R}{M_{A_2}}$

T temperature divided by $\dfrac{N_0 D}{R}$

t time

u flow speed divided by $\sqrt{\dfrac{N_0 D}{M_{A_2}}}$

x mass fraction of gas dissociated, $\dfrac{n_A}{2n_{A_2}+n_A}$

y distance along the flow

γ derivative along the flow direction of $\dfrac{d\log p}{d\log \rho}$

ϵ vibrational energy per molecule, $\epsilon(T)=\theta\left[\exp\left(\dfrac{\theta}{T}\right)-1\right]^{-1}$

ν vibrational frequency of molecule

λ relaxation distance

ρ density divided by C

θ number characteristic of a particular species of molecule, $\dfrac{h\nu}{D}$

μ constant (see eq. (21))

6

Subscripts

A   molecule of type O or N

A_2 molecule of type O_2 or N_2

c   chemical

D   dissociation

e   electronic

rot   rotational

tr   translational

v   vibrational

1,2,3   value of variables at a particular point in the flow (see sketch (b))

o   initial value

Superscripts

′   dimensional variable

·   time derivative

I. THE BASIC EQUATIONS AND CONCEPTS

Limitations of Present Analysis

The problem will be restricted to one-dimensional steady-state flow (assumption 1). Thus, it would apply to channel flow or to flow along a streamtube, where the cross-sectional area of the tube is regarded as a variable. The nature of the approximation involved in the treatment of a physical flow as one-dimensional is discussed in books on aerodynamics. Some of the present results are directly applicable to two- and three-dimensional flow, while others apply only to the one-dimensional flow. The extension of the results to two- and three-dimensional flow is beyond the scope of the present paper (see section entitled "Application of Foregoing Results - Extension of Theory to Air").

The analysis is further restricted by the assumption of an explicit model for the gas in question (assumption 2). It is assumed that we are

dealing with a pure homonuclear diatomic gas, which is subject to harmonic molecular vibrations, and which is undergoing the dissociation-recombination reaction $A_2 \rightleftarrows 2A$. This model would, for example, be correct for pure N_2 or pure O_2. Under a rather wide range of circumstances, to be examined later, it yields results directly applicable to air. The molecules are treated as independent particles, so that the attractive intermolecular forces responsible for liquefaction are ignored. This is a satisfactory assumption except at such low temperatures and high pressures that the gas is near to condensation.

In the present model of the gas, the small effects arising from vibration-rotation coupling and anharmonic vibrations are not included. In addition, the simplifying assumption is made that changes in electronic excitation do not occur. At very high temperatures this last assumption is not valid because the probability of any particular molecular species being electronically excited (relative to not being excited) is approximately given by the Boltzmann factor[1] $\exp(-\theta_e/T)$, where θ_e is a temperature characteristic of the species. For atomic oxygen and nitrogen the characteristic temperatures are $22,710^\circ$ K and $27,610^\circ$ K, respectively, while for molecular oxygen and nitrogen they are $11,340^\circ$ K and $71,575^\circ$ K, respectively. (In figs. 1 and 2 the fraction of internal energy in electronic excitations is shown graphically for various species and for air.)

Finally, viscosity, heat conduction, diffusion, radiation, and the possible formation of shock waves are neglected in the present analysis (assumption 3). The only entropy-producing mechanisms are the vibrational and chemical relaxations.

Mathematical Description of the Gas
(Internal Energy and Equation of State)

The nature of the gas is fully specified by the expression for the internal energy of the gas together with the equation of state. In mathematical language the model of the gas will consist of these two equations, which will embody assumption 2. Since these equations characterize the gas, and not any particular flow, they are not restricted to one-dimensional analysis and do not involve assumptions 1 and 3.

To write the expression for the internal energy of the gas, two additional variables are introduced, the vibrational energy per gram of gas, e_v', and the degree of dissociation defined by $x = n_A/2n_{A_2}+n_A$. Here x is the mass fraction of A in atomic form.

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[1] In the estimation of the error introduced by neglecting the electronic excitation of a molecule, it is noted that at equilibrium the ratio of electronic energy per molecule to its translational energy is of the order $(\theta_e/T)\exp(-\theta_e/T)$, falling off _less_ rapidly with increasing θ_e/T than the $\exp(-\theta_e/T)$ factor alone.

The internal energy per gram of gas, as calculated from elementary statistical mechanics, consists of "random" translational motion[2] $e_{tr}'=(3RT'/2M_{A_2})(1+x)$, rotational energy $e_{rot}'=(RT'/M_{A_2})(1-x)$, vibrational energy e_v', and energy due to dissociation $e_D'=(N_oD/M_{A_2})x$. The electronic energy is neglected, as is stated in assumption 2 above.

With only this approximation the internal energy per gram of gas is

$$e'=e_v'+e_{tr}'+e_{rot}'+e_D'=e_v' + \frac{RT'}{M_{A_2}} \frac{5+x}{2} + \frac{N_oD}{M_{A_2}} x \tag{1}$$

The equation of state of the gas is

$$\frac{p'}{\rho'} = (1+x) \frac{RT'}{M_{A_2}} \tag{2}$$

Equation (2) does not require chemical equilibrium nor vibrational equilibrium. The temperature T' is the temperature of the random translational motion of the molecules and may not be at all characteristic of the vibrational motion. The pressure of the gas comes from translational motion only. Following Lighthill (ref. 5), we introduce convenient dimensionless variables $T=RT'/N_oD=T'/\theta_D$, $e_v=e_v'M_{A_2}/N_oD$, and $e=e'(M_{A_2}/N_oD)$. In terms of these variables, equation (1) becomes

$$e=e_v+x+T\left(\frac{5+x}{2}\right) \tag{3}$$

and the dimensionless enthalpy[3] $h=e+(M_{A_2}/N_oD)(p'/\rho')$ is from equations (2) and (3)

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[2]The word "random" unfortunately suggests that the motion of these molecules is chaotic, following no fixed laws of motion. What is meant is that the detailed motion of the individual molecules is not specified; nor are these detailed motions relevant for the present calculations, since only average statistical quantities are needed, such as the average energy per molecule. The word "random" is used to distinguish these individual molecular motions from the collective drift or flow of the gas.

[3]The quantity h/T is equal to the usually tabulated quantity H/RT, where H is the enthalpy per mol of gas.

$$h = e_v + x + T\left(\frac{7+3x}{2}\right) \tag{4}$$

In the simple expressions (3) and (4) only assumption 2 is made, and no other simplifying assumptions are made, such as those by Lighthill (ref. 5) in treating equilibrium flow, and by Freeman (ref. 6). Freeman treats the flow behind a shock wave, making the simplifying assumption that the vibrational energy e_v is equal to exactly half of the classical equilibrium value and dissociation is the only relaxation phenomenon. Their assumptions lead to a value of $\gamma = 4/3$ at low temperatures, while the present model leads to the correct value of $7/5$.

Differential Flow Relations

For steady one-dimensional flow, in which friction forces and heat conduction are neglected (assumptions 1 and 3), the conservation equations derived in books on aerodynamics are

$$u'du' + dh' = 0 \qquad \text{(energy)} \tag{5}$$

$$u'du' + \frac{dp'}{\rho'} = 0 \qquad \text{(momentum)} \tag{6}$$

$$d(\rho'u'A) = 0 \qquad \text{(mass)} \tag{7}$$

These first two can be combined to give the implicit condition that no heat is added to the system:

$$0 = dh' - \frac{dp'}{\rho'} = de' + p'd\left(\frac{1}{\rho'}\right) \tag{8}$$

The bulk of the subsequent analysis consists in particular applications of the flow equations (5) to (8) to a gas whose energy, enthalpy, and equation of state are given by equations (3), (4), and (2), respectively. For this analysis it will be useful to write the flow equations (5) and (8) in the more explicit form obtained by inserting the expressions (3) and (4):

$$u \, du + de_V + \left(1 + \frac{3}{2} T\right) dx + \left(\frac{7+3x}{2}\right) dT = 0 \tag{9}$$

$$de_V + \left(1 + \frac{T}{2}\right) dx + \frac{5+x}{2} dT - (1+x) T \frac{d\rho}{\rho} = 0 \tag{10}$$

Here the dimensionless measure of velocity $u = u' \sqrt{M_{A_2}/N_O D}$ has been introduced. The unit of velocity $\sqrt{N_O D/M_{A_2}}$ represents approximately the average speed of random thermal motion of gas molecules at the temperature corresponding to the dissociation energy of the molecule. This average speed of gas molecules is always approximately equal to the sound speed at the same temperature.

Equation (9) simply expresses the constancy of the total enthalpy along the streamtube in terms of the four variables u, e_V, x, and T. Similarly, equation (10) expresses the condition of zero heat addition to the system during the flow.

The Local Polytropic Exponent

In many aerodynamic applications, the quantity $\gamma = (d \log p)/(d \log \rho)$ plays an important role, where dp and $d\rho$ are taken as the actual pressure and density variation along the flow. For this reason we give here the general expression for γ in terms of the variables used above:

$$\gamma = \frac{dh}{de} = \frac{(7+3x)+(2+3T) \frac{dx}{dT} + 2 \frac{de_V}{dT}}{(5+x)+(2+T) \frac{dx}{dT} + 2 \frac{de_V}{dT}} \tag{11}$$

The derivatives appearing in equation (11) refer to the actual process the gas is undergoing. The quantity γ has from its definition the significance of a local polytropic exponent.

For nonreacting gases with constant specific heats it is well known that γ is equal to the ratio of specific heats C_p and C_ρ. The equality $\gamma = C_p/C_\rho$ is also true for a chemically inactive gas in vibrational equilibrium. It does not hold, however, in a chemically reactive gas. In nonequilibrium problems, C_p and C_ρ are not even uniquely defined.

A further property of γ in a nonreacting, nonvibrating gas is its relation to the speed of sound $\gamma(p/\rho)=a^2$. We shall not here enter into the question: In what, if any, sense does $\sqrt{\gamma(p/\rho)}$ represent the sound speed in a relaxing medium? The question is an involved one because vibrating and dissociating air is a dispersive medium (ref. 14); the problem is outside the scope of a paper on steady flow.

In one-dimensional flow, however, the speed, $\sqrt{\gamma(p/\rho)}$, does have in any case one special significance; namely, it is a direct consequence of basic equations (6) and (7) that at a throat of a nozzle, unless $dp'=0$, the flow velocity is related to γ by

$$u_{throat} = \sqrt{\gamma(p/\rho)} \tag{12}$$

This result is valid for nonequilibrium flow as well as isentropic flow.

The Entropy in Nonequilibrium Flow

As was mentioned earlier, the right-hand side of equation (10) is the heat added to the system. It is readily verified that dividing equation (10) by the temperature T does not yield an exact differential, so that the right-hand side may not generally be written as $T\,dS$. In nonequilibrium flow, entropy may be produced within the system without any heat exchange with the surroundings.

In the theory of irreversible processes, the concept of entropy is generalized to include nonequilibrium phenomena. Rather general formulas for the entropy are given in books on the theory of irreversible processes and also in reference 12. In order to apply the theory to the vibrating-dissociating gas out of equilibrium, the assumptions must be made that the vibrations may be thought of as being in equilibrium with themselves, so that they can be characterized by a vibrational temperature T_v. In equilibrium flow this temperature coincides with the translational temperature T of the gas but, in general, it has a different value. This temperature is related to the vibrational energy per diatomic molecule by the formula

$$\epsilon(T_v) = \frac{\theta}{e^{\theta/T_v}-1} \tag{13a}$$

or by its inverse:

$$\frac{\theta}{T_v} = \log\left(1 + \frac{\theta}{\epsilon}\right) = \log\left[1 + \frac{\theta(1-x)}{e_v}\right] \tag{13b}$$

The expression (13a) results when an assembly of harmonic oscillators is assumed to be distributed in a Boltzmann distribution at a temperature T_v.

Evaluation of the entropy of the gas whose internal energy and equation of state are given by equations (1) and (2), respectively, yields (see appendix A):

$$dS = \frac{de_v}{T_v} + \frac{x+5}{2}\frac{dT}{T} - (1+x)\frac{d\rho}{\rho} + \left[\log\frac{(1-x)\sqrt{T}(1-e^{-\theta/T_v})}{\rho x^2} + \frac{1}{2}\right]dx \tag{14}$$

To verify that S is indeed an exact differential of the four variables, T, ρ, x, and e_v, one only needs to replace θ/T_v in equation (14) by its expression in terms of x and e_v (eq. (13b)). For a gas in equilibrium $T_v=T$, and x is determined by the equilibrium constant so that

$$\log\frac{(1-x)\sqrt{T}(1-e^{-\theta/T})}{\rho x^2} = \frac{1}{T}$$

and the right-hand side of equation (14) reduces to the left-hand side of equation (10) divided by T. For this to be true, it is necessary to use a unit of density which depends on the gas $\rho=\rho'/C$, as is discussed in appendix A. This constant density C for different gases is listed in appendix B.

Since the function S of equation (14) correctly represents the entropy in nonequilibrium flow only when the vibrations are distributed in a Boltzmann distribution, some comment about the distribution of vibrational energy levels is in order. Detailed investigations of this point have been made by Montoll, Rubin, and Schuler (refs. 15, 16, and 17). Their results show that in the situations usually encountered in gasdynamic problems, vibrational levels will be populated according to a Boltzmann distribution, characterized by a time-dependent vibrational temperature. The one circumstance in which significant deviations are expected to occur is when a fast chemical reaction is depleting or filling certain vibrational levels preferentially. This can occur only when the chemical relaxation time is short compared to the vibrational relaxation time. Fortunately, when the reaction is fast and many molecules are dissociating or recombining, the energy changes involved in the reaction are very large compared to the energy changes involved in vibrational

relaxation. (The relative amount of energy involved is of the order of θ_D/θ_v, see appendix B.) Consequently, just in these cases one expects no serious error to result in flow problems from a very approximate treatment of the vibrations.

Adiabatic Flow

For adiabatic flow the expression for the entropy change is obtained by combining the condition (10), no heat exchange with the surroundings, with the general expression for the entropy, equation (14). The resulting entropy change will then be entirely due to the irreversible relaxation processes:

$$dS=de_v\left(\frac{1}{T_v}-\frac{1}{T}\right)+dx\left[\log\frac{(1-x)\sqrt{T}(1-e^{-\theta/T_v})}{\rho x^2}-\frac{1}{T}\right] \tag{15}$$

According to the postulates of the theory of irreversible processes the expression (15) is always positive or zero for any actual physical process. In the usual language and notation of that theory, de_v/dt and dx/dt are "fluxes" (J_v, J_c) and the coefficients of de_v and dx in equation (15) are the corresponding "forces" (X_v, X_c). The quantity

$$T\log\frac{(1-x)\sqrt{T}(1-e^{-\theta/T_v})}{\rho x^2}-1=T\log\frac{e^{-1/T}\sqrt{T}(1-e^{-\theta/T_v})(1-x)}{\rho x^2}$$

is the "affinity" (A) of the reaction, a measure of the deviation from chemical equilibrium. For any well-defined flow the theory yields a relationship between the vibrational relaxation rate $\dot{e}_v$ and the rate of reaction $\dot{x}$, known as the Onsager reciprocal relation

$$\left.\frac{\partial\dot{x}}{\partial X_v}\right)_{eq}=\left.\frac{\partial\dot{e}_v}{\partial X_c}\right)_{eq} \tag{16}$$

The subscript eq means that the derivatives are taken at the equilibrium value. This relation may become useful when one, for example, has knowledge of vibrational relaxation rates for gases not in complete chemical equilibrium, for then equation (16) gives information about the reaction rate in flows where the vibrations are out of equilibrium. Were

it not for the high activation energy of the dissociation reaction, the equation (16) could be replaced by a linear algebraic relation between the forces and the fluxes.

The Heat Flow Analogy

When there are two heat reservoirs, one at a temperature T_I and the other at a temperature T_{II}, and energy flows between them, system I changing its energy by an amount de; then the entropy increase is

$$dS = de\left(\frac{1}{T_I} - \frac{1}{T_{II}}\right) \tag{17}$$

This quantity is always positive because the heat flow is always from higher to lower temperature.

Comparison of equations (15) and (17) suggests that the relaxation process is quite analogous to heat flow, energy being interchanged between the "system of vibrations" at temperature T_v; the "system of translational motions" at temperature T; and the "chemical system" at a temperature $\left[\log \dfrac{(1-x)\sqrt{T}(1-e^{-\theta/T_v})}{\rho x^2}\right]^{-1}$.

At equilibrium these three temperatures would all coincide. This analogy is quite correct when only the vibrations are relaxing and no reaction is occurring. However, when reaction is occurring the analogy can be quite misleading, because the quantity $\left[\log \dfrac{(1-x)\sqrt{T}(1-e^{-\theta/T_v})}{\rho x^2}\right]^{-1}$ cannot really be regarded as a chemical temperature, since its value depends not only on the chemical system, but also on the vibrations (T_v) and the translations (T); so it is seen that while the chemical affinity plays a role similar to that of a temperature difference, it is in some respects quite different from a temperature difference.

Explicit Form of the Entropy Function

A consequence of the existence of the entropy function is that equation (14) can be integrated from some initial (0) point to some final point along an arbitrary path of integration in the four-dimensional x, e_v, ρ, T space. Varying only one variable at a time in the order x, e_v, ρ, T gives, with the help of equation (13b),

$$S-S_O=\left[\frac{3}{2} + \log \frac{1-x_O}{\rho_O x_O{}^2} (1-e^{-\theta/T_{VO}})\sqrt{T_O}\right](x-x_O)+2x \log\left(\frac{x_O}{1-x_O} \frac{1-x}{x}\right)+\left(\frac{\sigma}{T_V} - \frac{\sigma_O}{T_{VO}}\right)+$$

$$(1-x)\log \frac{\epsilon}{\epsilon_O} - (1+x)\log \frac{\rho}{\rho_O} + \frac{5+x}{2} \log \frac{T}{T_O} \tag{18}$$

with $\sigma=e_V+\theta(1-x)$ and $\sigma_O=e_{VO}+\theta(1-x)$. The first four terms of equation (18) arise from the change in x and from the variation in vibrational energy, and the last two terms arise because of the density and temperature change. The expression (18) thus gives the entropy in a vibrating-reacting gas regardless of whether it is in equilibrium or not. The familiar expression for entropy, when no vibrations and no reaction is occurring, is obtained from equation (18) when $e_V=e_{VO}$ and $x=x_O$. A more compact way of writing equation (18) is

$$S-S_O=\left[\frac{3}{2} + \log \frac{1-x_O}{\rho_O x_O{}^2} (1-e^{-\theta/T_{VO}})\sqrt{T_O}\right](x-x_O)+\left(\frac{\sigma}{T_V} - \frac{\sigma_O}{T_{VO}}\right)+$$

$$\log\left[\left(\frac{x_O}{1-x_O} \frac{1-x}{x}\right)^{2x} \left(\frac{\epsilon}{\epsilon_O}\right)^{1-x} \left(\frac{\rho_O}{\rho}\right)^{1+x} \left(\frac{T}{T_O}\right)^{\frac{5+x}{2}}\right]$$

This dimensionless measure of the entropy is equal to the entropy per mole of gas divided by the universal gas constant R.

II. ISENTROPIC FLOW

Types of Isentropic Flow

The condition that adiabatic flow be also isentropic is seen from equation (15) to be

$$de_V\left(\frac{1}{T_V} - \frac{1}{T}\right)+dx\left[\log \frac{1-x}{\rho x^2} \sqrt{T}(1-e^{-\theta/T_V}) - \frac{1}{T}\right]=0 \tag{19a}$$

This isentropic condition may be written in a different form by introducing the relation

$$e_V=(1-x)\epsilon$$

where ϵ is the vibrational energy per diatomic molecule. By use of ϵ and x as independent variables the condition becomes

$$(1-x)d\epsilon\left(\frac{1}{T_v} - \frac{1}{T}\right)+dx\left[\log \frac{1-x}{\rho x^2} \sqrt{T}(1-e^{-\theta/T_v}) - \frac{1}{T} + \epsilon\left(\frac{1}{T} - \frac{1}{T_v}\right)\right]=0$$

(19b)

By inspection of equations (19a) and (19b) the different kinds of isentropic flow can be listed.

(1) Frozen flow, $de_v=0$ and $dx=0$. In a flow problem this corresponds to low temperatures or relaxation lengths much longer than the physical dimensions in the problem.

(2) Full equilibrium flow; $T_v=T$ and

$$\frac{\rho x^2}{1-x} = e^{-1/T} \sqrt{T}(1-e^{-\theta/T}) \equiv K(T)$$

(20)

The right-hand side of this expression is the equilibrium constant of the reaction. This condition is satisfied when the relaxation lengths are very short compared to the physical dimensions of the problem.

(3) Vibrational equilibrium, but the reaction is frozen; $T_v=T$ and $dx=0$. This flow occurs either at temperatures sufficiently low that dissociation is negligible, or when the chemical relaxation length is very long. In either case, the vibrational relaxation length must be short compared to the physical dimensions.

(4) Chemical equilibrium, but vibrational energy constant;

$$de_v=0$$

and

$$\frac{\rho x^2}{1-x} = e^{-1/T}(1-e^{-\theta/T_v})\sqrt{T}$$

This isentropic flow requires the condition

$$de_V = (1-x)d\epsilon - \epsilon\,dx = 0$$

In microscopic terms, whenever diatomic molecules dissociate, some other diatomic molecules in the system will gain an amount of vibrational energy (on the average) equal to the amount that the dissociating particle had before it broke up. This appears physically unlikely, and it is concluded that this type of flow does not occur.

(5) Chemical equilibrium, but vibrational temperature constant; $dT_V=d\epsilon=0$

$$\frac{\rho x^2}{1-x} = \mu\sqrt{T}\,e^{-\frac{1-\epsilon}{T}} \equiv K'(T,T_V) \tag{21}$$

with the constant

$$\mu = e^{-\epsilon/T_V}(1-e^{-\theta/T_V})$$

Comparison of equations (20) and (21) shows that the equilibrium constant is different in full equilibrium flow than in the case of constant vibrational temperature. This type of flow is physically much more reasonable than the case (4).

We now proceed to evaluate and list a number of relationships between flow variables for the cases (1), (2), (3), and (5), in particular for one-dimensional channel flow.

Frozen reaction and frozen vibrations.- First the case is considered, where the chemical reaction may be regarded as frozen at some arbitrary degree of dissociation, x_0, and the vibrations are frozen at an arbitrary vibrational energy e_{V0}. This is of course the usual case of constant specific heat,

$$c_V = \frac{5+x}{2}, \qquad c_p = \frac{7+3x}{2}, \qquad \gamma = \frac{7+3x}{5+x}$$

but is included here as a special case. Equation (14) becomes

$$\frac{5+x}{2} \frac{dT}{T} = (1+x) \frac{d\rho}{\rho}$$

giving

$$\frac{T}{T_O} = \left(\frac{\rho}{\rho_O}\right)^{\frac{2+2x_O}{5+x_O}} \tag{22a}$$

For a pure diatomic gas, the exponent is $2/5$ and for a pure monatomic gas it is $2/3$. Using equations (2) and (9), one readily has the further relationships

$$\frac{p}{p_O} = \left(\frac{T}{T_O}\right)^{\frac{7+3x_O}{2+2x_O}} = \left(\frac{\rho}{\rho_O}\right)^{\frac{7+3x_O}{5+x_O}} \tag{22b}$$

$$u^2 - u_O^2 = (7+3x_O)(T_O - T) \tag{22c}$$

$$\frac{A}{A_O} = \left(\frac{T_O}{T}\right)^{\frac{5+x_O}{2+2x_O}} \frac{u_O}{\sqrt{u_O^2 + (T_O - T)(7+3x_O)}} \tag{22d}$$

For any given channel shape $A(y)$, equations (22) give the temperature, pressure, velocity, and density distribution. The entropy is from equation (14) given by

$$S = -(1+x)\log \rho + \frac{5+x}{2} \log T + \text{constant} \tag{22e}$$

Frozen reaction - vibrations in equilibrium.- The next simplest case is the one in which the reaction is frozen at some arbitrary degree of dissociation x_O, and the vibrations are in equilibrium with the random translations. The dimensionless vibrational energy of the gas is then given by[4]

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[4] Here the usual harmonic oscillator approximation for the vibrations is made (see, e.g., ref. 18).

$$e_V = (1-x)\epsilon \tag{23}$$

with

$$\epsilon(T) = \frac{\theta}{e^{\theta/T}-1} \xrightarrow[\theta/T\ll1]{} T - \frac{\theta}{2} \tag{23a}$$

The number $\theta = \theta_V/\theta_D$ is a constant characteristic of the gas and is equal to $h\nu/D$, where $h\nu$ is the energy of a vibrational quantum of the gas, and D is the dissociation energy. Inserting equation (23) into equation (14) readily verifies that the entropy is a unique function of T and ρ. Integration of equation (14) and of equation (9) after the expression (23) is inserted for e_V, gives with the help of the equation of state (2) the following relationships:

$$\frac{p}{p_O} = \left(\frac{T}{T_O}\right)^{\frac{7+3x_O}{2+2x_O}} \exp\left(\frac{1-x_O}{1+x_O} J\right) \tag{24a}$$

$$\frac{\rho}{\rho_O} = \left(\frac{T}{T_O}\right)^{\frac{5+x_O}{2+2x_O}} \exp\left(\frac{1-x_O}{1+x_O} J\right) \tag{24b}$$

$$u^2 - u_O^2 = (T_O - T)(7+3x) + 2(e_{VO} - e_V) \tag{24c}$$

$$\frac{A}{A_O} = \left(\frac{T_O}{T}\right)^{\frac{5+x_O}{2+2x_O}} \exp\left(- \frac{1-x_O}{1+x_O} J\right) \frac{u_O}{\sqrt{u_O^2 + (T_O - T)(7+3x) + 2(e_{VO} - e_V)}} \tag{24d}$$

where J is defined by

$$J = \int_{\theta/T}^{\theta/T_o} \frac{ze^z dz}{(e^z-1)^2} = \log \frac{e^{\theta/T_o}-1}{e^{\theta/T}-1} + \frac{\theta}{T} \frac{1}{1-e^{-\theta/T}} - \frac{\theta}{T_o} \frac{1}{1-e^{-\theta/T_o}}$$

(25)

The specific heat is given also by differentiation of equations (3) and (4), respectively,

$$C_v = \left.\frac{\partial e}{\partial T}\right)_\rho = \frac{5+x_o}{2} + (1-x_o) \frac{d\epsilon}{dT}$$

(26a)

$$C_p = \left.\frac{\partial h}{\partial T}\right)_p = \frac{7+3x_o}{2} + (1-x_o) \frac{d\epsilon}{dT}$$

(26b)

Because e and h are functions of temperature only, the ratio of specific heats equals γ, defined by equation (11), giving

$$\gamma = \frac{7+3x_o+2(1-x_o) \frac{d\epsilon}{dT}}{5+x_o+2(1-x_o) \frac{d\epsilon}{dT}}$$

(26c)

Instead of the usual relation, $C_p-C_v=1$, it is found that

$$C_p-C_v=(1+x_o)$$

(26d)

as is evident from equations (26a) and (26b). The expression for $d\epsilon/dT$ required in equations (26a), (26b), and (26c) is obtained from equation (23):

$$\frac{d\epsilon}{dT} = \left(\frac{\epsilon}{T}\right)^2 e^{\theta/T} \xrightarrow[\theta/T \ll 1]{} 1$$

(27)

The frequently occurring oscillator function ϵ/T and the derivative $d\epsilon/dT$ are tabulated in reference 18, pages 445-447.

The entropy is found from equation (14) to be, for adjacent stream-lines,

$$S = -(1+x_O)\log \rho + \frac{5+x}{2} \log T + (1-x_O)\left(\frac{\epsilon+\theta}{T} + \log \epsilon\right) + \text{const} \qquad (28)$$

When

$$\frac{\theta}{T} \gg 1 \quad \text{and} \quad \frac{\theta_O}{T_O} \gg 1 \qquad (29)$$

then $J=0$, and $e_V=0$, and the expressions (24) reduce to equations (22). This must be so because at sufficiently low temperatures no vibrations are excited and there is no difference between frozen and equilibrium vibrations. In addition, when the opposite conditions, namely,

$$\frac{\theta}{T} \ll 1 \quad \text{and} \quad \frac{\theta_O}{T_O} \ll 1 \qquad (30)$$

are satisfied, then the relatively complicated expressions (24) become simple again. Expressions (23) and (27) give $J=\log T/T_O$ at high temperatures. Then the formulas (24) reduce to those of a gas with constant specific heats

$$C_V = \frac{7-x_O}{2} , \qquad C_p = \frac{9+x_O}{2} , \qquad \gamma = \frac{9+x_O}{7-x_O} \qquad (31)$$

These expressions are

$$\frac{p}{p_O} = \left(\frac{T}{T_O}\right)^{\frac{9+x_O}{2+2x_O}} = \left(\frac{\rho}{\rho_O}\right)^{\frac{9+x_O}{7-x_O}} \qquad (32a)$$

$$u^2 - u_O^2 = (T_O - T)(9+x) \qquad (32b)$$

$$\frac{A}{A_O} = \left(\frac{T_O}{T}\right)^{\frac{7-x_O}{2+2x_O}} \frac{u_O}{\sqrt{u_O{}^2 - (9+x_O)(T-T_O)}} \tag{32c}$$

Equations (32) are very similar in form to equations (22). When $x_O=1$ they are identical because when the gas is completely dissociated, the vibrational energy is zero. On the other hand when $x_O=0$ (no dissociation), the effect of vibrations at high temperatures is to change γ from 7/5 to 9/7. The approximation introduced by Lighthill (ref. 5) involves using $\gamma=(4+x_O)/3$, leading to $\gamma=4/3$ in the case of no dissociation. This value is intermediate to $\gamma=7/5$ (condition (29)) and $\gamma=9/7$ (condition (30)). Lighthill's approximation corresponds to replacing ϵ by $T/2$. His approximation is better than equations (22) or (32) for the temperature range $\theta/2 < T < \theta$, while equations (32) are better than Lighthill's result whenever $T > \theta$, and equations (22) are better when $T < \theta/2$. Equations (32) never underestimate the deviations from the frozen vibrations but, at temperatures close to θ or smaller than θ, overestimate the effect of vibrations on the flow. Equations (24), on the other hand, cover the whole temperature range.

The approximations (29) and (30) depend on the magnitude of θ/T. A characteristic temperature is defined as $\theta_V=h\nu/k$, so that $\theta_V/T'=\theta/T$, and the value of this characteristic temperature is listed in the table in appendix B. It also gives M_{A_2} and D/k, the constants needed to convert dimensional quantities (e', T', etc.) to dimensionless quantities (e, T, etc.).

Reaction in equilibrium - vibrational temperature constant.- In this case the analytic formulas are more complicated because the equilibrium value of x is given by the relatively complicated equation

$$K(T,T_V) \equiv \frac{\rho x^2}{1-x} = \mu \sqrt{T} \, e^{-\frac{1-\epsilon}{T}} \tag{21}$$

with

$$\mu = e^{-\epsilon/T_V}(1-e^{-\theta/T_V})$$

Here T_V and ϵ, and consequently μ, are constants which indicate the degree of vibrational excitation at which the gas remains frozen. When no vibrations are excited, then $\mu=1$ and $\epsilon=0$. The quantity ρ is

dimensionless. It is the physical density divided by the constant density C characteristic of the gas (appendix B). Solving equation (21) for ρ gives

$$\rho = \frac{1-x}{x^2} \mu \sqrt{T} \, e^{-\frac{(1-\epsilon)}{T}} \tag{33}$$

Since the entropy is an exact differential, equation (33) can be inserted into (14) with $dT_V=0$, and a two-variable relation can be obtained between x and T by integration. Inserting equation (33) into (14) gives the relation:

$$0=dS=\left[\frac{2(1-\epsilon)+T}{2T} - \frac{(1+x)(x-2)}{x(1-x)}\right]dx+\left[\frac{2}{T} - \frac{(1+x)(1-\epsilon)}{T^2}\right]dT \tag{34}$$

Integration of equation (34) yields

$$S = \frac{(1+x)(1-\epsilon)}{T}+\frac{3}{2} x + 2 \log \frac{Tx}{(1-x)(1-\epsilon)} + \text{integration constant} \tag{35}$$

The equation (35) represents the entropy of the streamtube. Since one is always interested only in entropy differences we put the integration constant equal to zero. Since equation (35) is not readily solved for x as an explicit function of T, the implicit relation is shown graphically in figure 3(a). The ordinate shows the dimensionless temperature $T/1-\epsilon$ rather than physical temperature T' because the relation between x and T' depends on the specific gas used, while the relation between x and $T/1-\epsilon$ (eq. (35)) is universal. Each of the lines on figure 3 is an isentrope, so that a dissociating-recombining gas moving along a streamtube of variable cross section will always remain on one curve as its temperature changes. For a specific gas one may obtain the density corresponding to a certain temperature by looking up x in figure 1 and then using equation (33) to obtain the density. The pressure can then be obtained from the equation of state, (2); the velocity is calculated from equation (4) and the constancy of $(u'^2/2) + h$:

$$u^2 - u_0^2 = 2(1-\epsilon)(x_0-x)+7(T_0-T)+3(T_0 x_0 -Tx) \tag{36}$$

Finally, one obtains the cross-sectional area from equations (33) and (36), and the continuity equation:

$$\frac{A}{A_O} = \frac{x^2}{1-x} \frac{\rho_O u_O \exp\frac{1-\epsilon}{T}}{\mu\sqrt{T[2(1-\epsilon)(x_O-x)+7(T_O-T)+3(T_O x_O-Tx)+u_O{}^2]}}$$

$$= \frac{x^2}{1-x} \frac{\rho_O u_O}{K(T,T_v)} [2(1-\epsilon)(x_O-x)+7(T_O-T)+3(T_O x_O-Tx)+u_O{}^2]^{-\frac{1}{2}}$$

$$(37)$$

Unlike equations (22), (24), and (32), the formulas (36) and (37) involve three variables, not just two. This is because of the inability to solve equation (35) explicitly for x in terms of T. Thus, figure 3(a) or equation (35) must be used in conjunction with equations (36) and (37). When all molecules are in the vibrational ground state, then $\mu=1$ and $\epsilon=0$. In that case it is noted that like equation (35), equations (36) and (37) are universal in the sense that for given initial conditions they yield unique values for velocity and cross-sectional area for every temperature T, and these values are independent of the nature of the gas. The quantity γ is given by equation (11) if $d\epsilon/dT=0$ and the value of dx/dT, defined by equation (34), are inserted:

$$\gamma = \frac{(7+3x)+(2+3T-2\epsilon)\frac{dx}{dT}}{(5+x)+(2+T-2\epsilon)\frac{dx}{dT}}$$

$$(38)$$

The specific heats are from equations (3) and (4)

$$c_v = \left.\frac{\partial e}{\partial T}\right)_\rho = \frac{5+x}{2} + \left(1 + \frac{T}{2} - \epsilon\right)\left.\frac{\partial x}{\partial T}\right)_\rho$$

$$(39a)$$

$$c_p = \left.\frac{\partial h}{\partial T}\right)_p = \frac{7+3x}{2} + \left(1 + \frac{3}{2}T-\epsilon\right)\left.\frac{\partial x}{\partial T}\right)_p$$

$$(39b)$$

Their ratio does not equal γ because the temperature derivatives $\partial x/\partial T)_S$, $\partial x/\partial T)_\rho$, and $\partial x/\partial T)_p$ are not equal to each other. The derivatives are from equations (33) and (2):

$$\left.\frac{\partial x}{\partial T}\right)_\rho = \frac{x(1-x)}{2-x}\left(\frac{1}{2T} + \frac{1-\epsilon}{T^2}\right) \tag{40a}$$

$$\left.\frac{\partial x}{\partial T}\right)_p = \frac{x}{2}(1-x^2)\left(\frac{1-\epsilon}{T^2} + \frac{3}{2T}\right) \tag{40b}$$

Reactions and vibrations in equilibrium.- If the chemical reaction as well as the molecular vibrations are in equilibrium with the translational temperature, one obtains relations which combine the effects of equilibrium vibration and those of equilibrium chemistry. The analysis proceeds similarly to that of the previous section.

Instead of equation (21), the equilibrium constant is

$$K(T) = \frac{\rho x^2}{1-x} = \sqrt{T}\,(1-e^{-\theta/T})e^{-1/T} \tag{20}$$

The equilibrium constant, equation (20), could have been obtained by direct evaluation from statistical mechanics rather than from the entropy function. For such a derivation, see any textbook on statistical mechanics; appendix C of this report contains a discussion indicating what physical motions give rise to the various factors on the right-hand side of equation (20).

At low temperatures, where

$$\frac{\theta}{T} \gg 1 \tag{41}$$

equation (20) reduces to (21) with $\epsilon=0$. This is a rather uninteresting case because at such low temperatures the equilibrium vibrations are negligible, and the dissociation also is usually negligible. More useful is the opposite limit of high temperatures,

$$\frac{\theta}{T} \ll 1 \tag{42}$$

in which $1-e^{-\theta/T}=\theta/T$. The general expression for the density is in view of equation (20):

$$\rho = \frac{1-x}{x^2} \sqrt{T} \ (1-e^{-\theta/T})e^{-1/T} \tag{43}$$

At high temperatures, when equation (42) applies, equation (43) may be replaced by

$$\rho = \theta \ \frac{1-x}{x^2} \ \frac{e^{-1/T}}{\sqrt{T}} \tag{44}$$

The approximation made by Lighthill might be mentioned, which is

$$\rho = \text{const} \ \frac{1-x}{x^2} \ e^{-1/T} \tag{45}$$

Lighthill shows that for oxygen and nitrogen his "constant" is really a slowly varying function of temperature which is increasing for small T and decreasing for large T, and has a maximum in the neighborhood of the maximum of $\sqrt{T} \ (1-e^{-\theta/T})$, the coefficient used in equation (43).

Eliminating e_V and ρ from equation (14) by the use of equations (23) and (43), respectively, one obtains analogously to equation (34):

$$\left[\frac{2+T-2\epsilon}{2T} + \frac{(x+1)(2-x)}{x(1-x)} \right]dx + \left[\frac{2}{T} - \frac{(1+x)(1-\epsilon)}{T^2} + \frac{e^{\theta/T}(1-x)\epsilon^2}{T^3} \right]dT = dS = 0 \tag{46a}$$

Integrating the exact differential equation (46a) gives analogously to equation (35), if the integration constant is again put equal to zero,

$$S_O(\theta) = \frac{1+x}{T} + \frac{3}{2} x + 2 \log \frac{Tx}{1-x} + \frac{\epsilon}{T} (e^{\theta/T}-x) + \frac{\theta}{T} + 2 \log \frac{\epsilon}{\theta} \tag{47a}$$

For temperatures large compared to θ, the expression (47a) reduces to:

$$S_O = \frac{1+x}{T} + \frac{x}{2} + 2 \log \frac{T^2 x}{1-x} \tag{47b}$$

The entropy S_O of equations (47b) and (35) has a different zero level[5] than the $\bar{S}_O(\theta)$ of equation (47a). They are related by $S_O(\theta)=S_O+1-2 \log \theta$. While expression (47b) is independent of the nature of the gas (just as eq. (35)), expression (47a) does depend on θ, a number different for every gas. The relation (47a) is plotted for oxygen ($\theta=0.0367$) and nitrogen ($\theta=0.0291$) in figures 3(b) and 3(c), respectively. The insensitivity of the curves to the exact value of θ is evident, so that for practical purposes these curves may be regarded valid for either gas. Again the physical meaning of the curves is that of an isentrope, and equilibrium flow along a streamline is constrained to remain on one such curve. It is noted in figure 3 that for very high temperatures the gas will recombine again. The reason is that very high pressures correspond to these temperatures. The temperature at which the gas is maximally dissociated is obtained by differentiation of equation (47a) and is:

$$T^* = \frac{1+x}{4} \tag{48}$$

This temperature is indicated in figure 3(b). These are such high temperatures for oxygen and nitrogen that the ionization of the gas would invalidate all quantitative aspects of the present model, which considers only the dissociation reaction. For less strongly bound gases, such as the halogens, however, the characteristic temperature is sufficiently low that the present model of the gas applies at that temperature. If the vibrations are frozen, the maximum dissociation occurs at a temperature equal to two times T^*.

To obtain the density corresponding to a specific temperature, first obtain x from figure 3 or by use of equations (47), then obtain ρ from equation (43). Pressure then follows from the equation of state, (2). The velocity is, in view of the conservation of total energy,

$$u^2-u_O{}^2=2(x_O-x)+7(T_O-T)+3(T_O x_O-Tx)+2(e_{vO}-e_v) \tag{49a}$$

where $e_v=\theta(1-x)/e^{\theta/T}-1$; at high temperatures $e_v=(1-x)T$, giving

$$u^2-u_O{}^2=2(x_O-x)+9(T_O-T)+(T_O x_O-Tx) \tag{49b}$$

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[5]To compare with the tables of Treanor and Logan, it should be noted that they tabulate (S/R) which for oxygen (ref. 19) is $S_O(\theta)+24.30$ and for nitrogen (ref. 20) is $S_O(\theta)+24.07$.

The cross-sectional area is obtained from equations (20) and (49a):

$$\frac{A}{A_O} = \frac{x^2}{1-x} \cdot \frac{\rho_O u_O}{K(T) \sqrt{u_O{}^2+2(x_O-x)+7(T_O-T)+3(T_O x_O-Tx)+2(e_{vO}-e_v)}}$$

(50a)

A somewhat simpler expression arises for high temperatures when equations (49b) and (44) are used; one finds $\rho_O u_O/\rho u$ is

$$\frac{A}{A_O} = \frac{x^2}{1-x} \cdot \frac{e^{1/T} \sqrt{T} \, \frac{\rho_O u_O}{\theta}}{\sqrt{u_O{}^2+2(x_O-x)+9(T_O-T)+(T_O x_O-Tx)}}$$

(50b)

Equations (49) and (50) are to be used in conjunction with figure 2 or 3, or equations (47). The value of γ we obtain using equation (11) is

$$\gamma = \frac{7+3x+2(1-x)\frac{d\epsilon}{dT} + (2+3T-\epsilon)\frac{dx}{dT}}{5+x+2(1-x)\frac{d\epsilon}{dT} + (2+T-\epsilon)\frac{dx}{dT}} \xrightarrow[\frac{\theta}{T} \ll 1]{} \frac{9+x+(2+T)\frac{dx}{dT}}{7-x+(2-T)\frac{dx}{dT}}$$

(51)

The functions $\epsilon(T)$ and $d\epsilon/dT$ are given by equations (23) and (27), respectively.

The quantity dx/dT is given by equation (46a); at high temperatures $(T \gg \theta)$, it becomes:

$$\frac{dx}{dT} = \frac{1}{T^2}\left[\frac{2-x}{x(1-x)} - \frac{1}{T(1+x)} + \frac{1}{2(1+x)}\right]^{-1}$$

(46b)

Lastly, the specific heats are computed from equations (3) and (4)

$$C_\rho = \left.\frac{\partial e}{\partial T}\right)_\rho = \frac{5+x}{2} + \left(1 + \frac{T}{2} - \epsilon\right)\left.\frac{\partial x}{\partial T}\right)_\rho + (1-x)\frac{d\epsilon}{dT}$$

(52a)

$$C_p = \frac{\partial h}{\partial T}\bigg)_p = \frac{7+3x}{2} + \left(1 + \frac{3T}{2} - \epsilon\right)\frac{\partial x}{\partial T}\bigg)_p + (1-x)\frac{d\epsilon}{dT} \qquad (52b)$$

Here $d\epsilon/dT$ is given by equation (27), and the other required derivatives are from equations (44) and (2) for high temperatures.

$$\frac{\partial x}{\partial T}\bigg)_\rho = \frac{x(1-x)}{2-x}\left(\frac{1}{T^2} - \frac{1}{2T}\right) \qquad (53a)$$

$$\frac{\partial x}{\partial T}\bigg)_p = \frac{x}{2}(1-x^2)\left(\frac{1}{T^2} + \frac{1}{2T}\right) \qquad (53b)$$

For the intermediate temperatures $T\approx\theta$, the exact expressions are readily obtained from equation (43), but they will not be given here explicitly because they are long expressions. For N_2 or O_2, T is always much less than unity and the $1/T$ term is negligible compared to the $1/T^2$ or $1/T^{3/2}$ term in equations (53) and (40). If these terms are neglected, equations (53) and (40) are identical.

Application of Foregoing Results - Extension of Theory to Air

To test the accuracy of the equilibrium calculation, exact tables for thermodynamic properties of oxygen (ref. 19) were compared with the results of the equations of the present paper. The tables range from temperatures of 2000° K to 5000° K, and densities from 10^{-3} to ten times the standard sea-level density. The entropy (eq. (47a)) was found to agree better than within 1/2 percent over the whole range. Calculation of the degree of dissociation by solving equation (43) for x,

$$x = K/2\rho\left(\sqrt{1+4\rho/K} - 1\right)$$

gave the results shown in figure 4(a). The resulting enthalpy is compared in figure 4(b). The comparisons indicate that the neglect of vibrational anharmonicity, vibration-rotation coupling, and electronic energy do not introduce serious deviations below 5000° K.

Although we have considered one-dimensional flows, the foregoing results may be useful in two- and three-dimensional flow problems. All the relationships derived are valid along a line on which entropy is

constant and on which the total enthalpy is constant. The expressions for entropy, such as equations (35) and (47) - valid along one streamtube - may be used to compare the entropy on adjacent streamtubes. This permits the calculation of entropy gradients and vorticity in the flow field.

The foregoing analysis assumed a dissociating diatomic gas of only one species, and is strictly valid only for experiments using such a relatively simple gas. Examples would be N_2, O_2, Cl_2, Br_2, and I_2. Yet the result may be used with some modifications as an approximation for air. This is possible because there is a definite region of temperature and pressure in which the oxygen of the air is chemically active while the nitrogen is chemically inert in its diatomic form. There is another definite region of pressure and temperature in which the N_2 is chemically active and the oxygen is completely dissociated. (For a careful definition of these regions see ref. 21.) The interaction of O_2 with N_2 to form NO is relatively unimportant because NO gas has thermodynamic properties intermediate between N_2 and O_2, thus having only little effect on the isentropic behavior of air.

In the temperature and pressure ranges where nitrogen dissociation is unimportant, the degree of dissociation for oxygen is defined as

$$x_{O_2} = \frac{n_0}{2n_{O_2}+n_0} \tag{54}$$

Then the basic equations in the analysis, namely, equations (2), (3), and (4), and also the differential relations (9) and (10), remain valid, provided x is replaced everywhere by $0.23x_{O_2}$. The 0.23 occurs because oxygen of the air is assumed to be 23 percent of the total mass, and nitrogen 77 percent. Also, in this approximation the expressions for the equilibrium constant, equations (21), (20), and (44), apply. In these expressions x must simply be replaced by x_{O_2} and the density ρ by 0.23ρ (the density of oxygen). The complete equilibrium expression for vibrational energy is

$$e_v = 0.77\epsilon_{N_2}+0.23(1-x_{O_2})\epsilon_{O_2} \tag{55a}$$

where ϵ_{N_2} and ϵ_{O_2} are the functions defined by equation (23a), the vibrational energy per nitrogen molecule or per oxygen molecule, respectively. Use of the complete equilibrium expression for e_v would yield rather complicated expressions (see the already complex eqs. (24) and (47a)

for one species). A useful approximation to expression (55a) obtained by
ignoring the difference between ϵ_{N_2} and ϵ_{O_2} is

$$e_V = \epsilon(1-0.23x_{O_2}) \qquad (55b)$$

This differs from the vibrational energy of a pure species (eq. (23)) only
in the replacement of x by $0.23x_{O_2}$. The function ϵ is given by equa-
tion (23a). Here a reasonable value of θ is $\overline{\theta}=0.23\theta_{O_2}+0.77\theta_{N_2}$. At high
temperatures, $T\gg\theta$, the quantity ϵ is equal to T independent of θ,
and the expression (55b) becomes exact. With the approximation (55b) the
formula for the full-equilibrium entropy of air is:

$$S = \frac{1+0.23x_{O_2}+\epsilon(e^{\overline{\theta}/T}-0.23x_{O_2})+\overline{\theta}}{T}+\frac{3}{2}(0.23x_{O_2})+2\log\frac{\epsilon Tx_{O_2}}{\overline{\theta}}-1.23\log(1-x_{O_2})$$
$$(56)$$

When the dimensionless result is converted into engineering units, the
appropriate value of D/K is $59,000^\circ$ K (the dissociation energy of
oxygen), and the correct value for M_{A_2} is 29.0 (the mean molecular
weight of cold air).

Calculation for air in the range where the oxygen is almost completely
dissociated and the nitrogen is chemically active can also be carried
through. At first sight it would seem that at these high temperatures
one would have to include the electronic energies. Actually it is not
much of an error to neglect the electronic energies provided most of the
nitrogen is undissociated; when most of the nitrogen is dissociated the
error becomes important. The reason for this is that molecular nitrogen
remains in its ground state until extremely high temperatures, while
atomic nitrogen is more readily excited. In figure 1 are shown the percent
of energy in electronic form of each of the four species, O, O_2, N_2, and N,
as a function of temperature. Figure 2 gives the corresponding result
for air. For example, at atmospheric density at 7000° K, the fraction
of the energy in electronic form is, according to figure 2, about 1/2
percent, certainly not a prohibitive amount for approximate calculations.
At the high temperatures where electronic excitations contribute at
equilibrium, application of the present method would give the frozen
excitation limit for the flow. When nitrogen is dissociating and the
oxygen is in completely atomic form, we require

$$x_{N_2} = \frac{n_N}{2n_{N_2}+n_N} \qquad (57)$$

and the basic equations, analogous to equations (2), (3), and (4), are,
with $M=29.0$,

$$\frac{p'}{\rho'} = (1.23 + 0.77 x_{N_2}) \frac{RT'}{M} \tag{58}$$

$$e = e_v + \frac{T}{2}(5.23 + 0.77 x_{N_2}) + 0.77 x_{N_2} \tag{59}$$

$$h = e_v + \frac{T}{2}(7.69 + 2.31 x_{N_2}) + 0.77 x_{N_2} \tag{60}$$

The vibrational energy is due only to the nitrogen vibration and so its equilibrium value is of nearly the same form as the vibrational energy of a single species; that is, $e_v = 0.77(1 - x_{N_2}) \epsilon_{N_2}$. It is evident that an analysis of this situation for air, based on equations (58), (59), and (60), is no more complicated than the analysis of the single species based on equations (2), (3), and (4). The only difference lies in the different numerical coefficients in equations (58), (59), and (60). The resulting full equilibrium entropy for air is

$$S = \frac{1.23(1+\theta) - 0.77 x_{N_2} + 0.77 \epsilon (e^{\theta/T} - x_{N_2})}{T} + 2 \log \frac{T\epsilon}{\theta(1 - x_{N_2})} +$$

$$1.23 \log x_{N_2}{}^2 + \frac{3}{2}(0.77) x_{N_2}$$

III. NONEQUILIBRIUM FLOW

It is not possible to discuss nonequilibrium flow as generally as isentropic flow. The dimensions of the streamtube enter as a new variable, and explicit results can be obtained only for flow which is specified not only by its initial state but also by some further condition. The aim here is to illustrate the method by consideration of specific situations for which the isentropic solutions are known. We then suppose that instead of frozen or equilibrium flow, relaxation is taking place and ask, "How will the flow differ?" Even when the relaxation rates are specified, the answer is not unique. For a unique answer, the question must be modified to read: "Suppose an additional constraint is placed on the flow, how will the relaxing flow look?"

For example, in isentropic flow, in a shock tube of constant cross section, the pressure, density, and temperature will be constant downstream of the shock wave. Conversely, if in isentropic flow along a streamtube the pressure is constant, then all the other variables must be constant

along the tube. The tube will of necessity have constant cross section. In relaxing flow constant pressure, constant density, and constant cross section are generally incompatible. We can ask, however, "Given a constant cross section, what will the pressure and density variation be?" or, "Given constant pressure, what will be the shape of the streamtube?" (See fig. 5, to be discussed later.) A more general form of the required constraint would be knowledge of a channel shape $A(y)$ or of a pressure distribution $p(y)$. In references 7, 8, and 10 examples of relaxation with specific channel shapes are worked out in detail.

Relaxing Vibrations

Let us first choose the simplest case to illustrate the above remarks; namely, the case where there is no reaction, but the vibration is relaxing. Let us suppose that from a knowledge of the thermodynamic and flow properties without relaxation, we can estimate the vibrational relaxation rate, $\frac{de_V}{dy} = \frac{1}{u}\frac{de_V}{dt}$, as a function of y. From the basic equations in part I, the cross-sectional area is computed as a function of y, with the assumption that one of the other variables is constant. The area is related to the variables, density and velocity, of part I through the continuity equation which may be written in the form

$$-d \log A = \frac{d\rho}{\rho} + \frac{du}{u} \qquad (61)$$

By making use of equation (61), and by putting $x=0$ in the earlier equations (2), (3), and (4), as well as (9) and (10) which require adiabatic flow, one obtains:

$$\frac{d \log A}{dy} = -\frac{2}{7T}\frac{de_V}{dy} \qquad \text{(pressure constant)} \qquad (62a)$$

$$\frac{1}{A^2}\frac{d \log A}{dy} = -\frac{1}{5}\left(\frac{\rho_0}{m}\right)^2\frac{de_V}{dy} \qquad \text{(density constant)} \qquad (62b)$$

$$\frac{d \log A}{dy} = -\left(\frac{1}{T_0} - \frac{1}{u^2}\right)\frac{de_V}{dy} \qquad \text{(temperature constant)} \qquad (62c)$$

$$\frac{d \log A}{dy} = 0 \qquad \text{(cross-section constant)} \qquad (62d)$$

A particular application of equations (62) is to a gas which has just passed through a strong shock wave; vibrations are at first unexcited, but will become excited in the ensuing flow through collision over a distance λ which depends on the temperature and density. Whatever the distance may be, de_V/dy will be greater than 0 over some distance. From equations (62a) and (62b) it is obvious that if the pressure is constant, the streamtube must contract; similarly, if the density is constant, the streamtube contracts. On the other hand, if the temperature is constant and the free-stream Mach number is larger than 1.2, the streamtube has to expand. In isothermal flow a possible situation behind a very weak shock wave is a streamtube which contracts at first and then expands when the velocity is sufficiently reduced. These results may also be put in the inverse way: If geometrical or other considerations tell us that stream-tubes are expanding while there is vibrational relaxation, then neither constant density nor constant pressure can be a correct assumption, but constant temperature is not ruled out.

In figure 5 the streamtube cross sections are plotted on semilog paper as functions of e_V/T_3, where T_3 is the equilibrium temperature and M_1 is the free-stream Mach number. The subscripts 1, 2, and 3 are used to denote "free stream," "immediately behind the shock," and "at full equilibrium," respectively. At equilibrium e_V/T_3 is unity, while immediately behind the shock it is zero. If the vibrational energy e_V increases behind the shock approximately exponentially with distance, and this is rather typical behavior, the abscissa of figure 5 may be regarded as an approximate linear measure of distance behind the shock instead of a logarithmic measure of vibrational energy. Regarded in this way, it is clear that for a nonrelaxing flow all the curves in figure 5 would coincide with the straight line, labeled A.

The formulas for the flow of constant chemical composition behind a shock wave now are summarized with e_V as the independent variable for the different cases. These formulas are easily obtainable by integration of the differential flow relations of part I. Subscripts 2 and 3 refer to conditions immediately behind shock and at final equilibrium, respectively.

Constant density flow.-

$$\rho(y) = \rho_2$$

$$\frac{T(y)}{T_2} = \frac{p(y)}{p_2} = 1 - \frac{2}{5} \frac{e_V(y)}{T_2}$$

$$\frac{A(y)}{A_2} = \frac{u_2}{u(y)} = \left[1 + \frac{4}{5} \frac{e_v(y)}{u_2{}^2} \right]^{-1/2}$$

$$S(y) = S_2 + \varphi(e_v) - \frac{5}{2} \log \frac{T_2}{T}$$

where

$$\varphi(e_v) \equiv \frac{e_v}{\theta} \log \frac{e_v + \theta}{e_v} - \log \frac{e_v + \theta}{\theta}$$

Constant pressure flow.-

$$p' = p_2'$$

$$u = u_2$$

$$\frac{T(y)}{T_2} = \frac{A(y)}{A_2} = \frac{\rho_2}{\rho(y)} = 1 - \frac{2}{7} \frac{e_v(y)}{T_2}$$

$$S - S_2 = \varphi(e_v) - \frac{7}{2} \log \frac{T_2}{T}$$

Isothermal flow.-

$$T(y) = T_2$$

$$\frac{u(y)}{u_2} = \sqrt{1 - \frac{2e_v(y)}{u_2{}^2}}$$

$$\frac{\rho(y)}{\rho_2} = \frac{p(y)}{p_2} = \exp\left[\frac{e_v(y)}{T_2} \right]$$

$$\frac{A_2}{A(y)} = \sqrt{1 - \frac{2e_v(y)}{u_2{}^2} \exp\left[\frac{e_v(y)}{T_2}\right]}$$

$$S - S_2 = \varphi(e_v)$$

For isothermal flow, the vibrations may never be able to reach equilibrium, because only the kinetic energy $(1/2)u_2{}^2$ is available for conversion to vibrational energy.

Constant cross section.- For a fuller treatment of this case, including the reaction rate, see the following section. Here only some of the interesting relations are given when density is used as the independent variable $\rho = \rho(y)$.

$$A(y) = A_2$$

$$\frac{u}{u_2} = \frac{\rho_2}{\rho}$$

$$\frac{T}{T_2} = \frac{\rho_2}{\rho}\left[1 + \frac{u_2{}^2}{T_2}\left(1 - \frac{\rho_2}{\rho}\right)\right]$$

$$\frac{p}{p_2} = 1 + \frac{u_2{}^2}{T_2}\left(1 - \frac{\rho_2}{\rho}\right)$$

$$e_v = \frac{7}{2}(T_2 - T) + \frac{1}{2}\left(u_2{}^2 - \frac{m^2}{\rho^2}\right)$$

$$S - S_2 = \varphi(e_v) - \frac{7}{2}\log\frac{T_2}{T} - \log\left[1 + \frac{u_2}{T_2}\left(u_2 - \frac{m}{\rho}\right)\right]$$

The equation for $T(\rho)$ was obtained by elimination of the velocity and e_v from equations (7c), (9), and (10) which gave the differential equation

$$\frac{dT}{d\rho} + \frac{T}{\rho} = \frac{m^2}{\rho^3}$$

Integration leads to the above formula. This is the only one of the above formulas for which the derivation is not fairly obvious.

It is noted that the relation between p and ρ behind the shock is <u>not</u> of the polytrope form $p/p_2 = (\rho/\rho_2)^n$. For the corresponding result which includes finite reaction rates see equation (67).

<u>Relaxation length</u>.- To obtain some physical feeling for the manner in which the characteristic feature of relaxing flow, namely, its dependence on linear distance, disappears when the relaxation length is very long or very short, consider the simple example of constant pressure flow behind a normal shock wave, and a typical exponential relaxation:

$$e_V(y) = e_V^e \left[1 - \exp\left(-\frac{y}{\lambda} \right) \right]$$

$$\cong T \left[1 - \exp\left(-\frac{y}{\lambda} \right) \right]$$

where e_V^e is the equilibrium vibrational energy, which for strong shocks is approximately equal to the local temperature. Then the simple resulting behavior is (see sketch (a)):

$$\frac{T}{T_2} = \frac{A}{A_2} = \frac{\rho_2}{\rho} \approx \frac{1}{7} \left(5 + 2e^{-y/\lambda} \right) \tag{63}$$
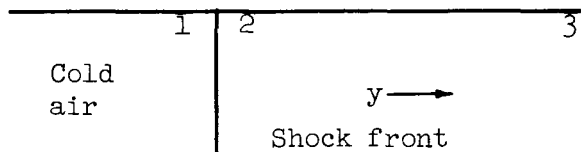

Sketch (a)
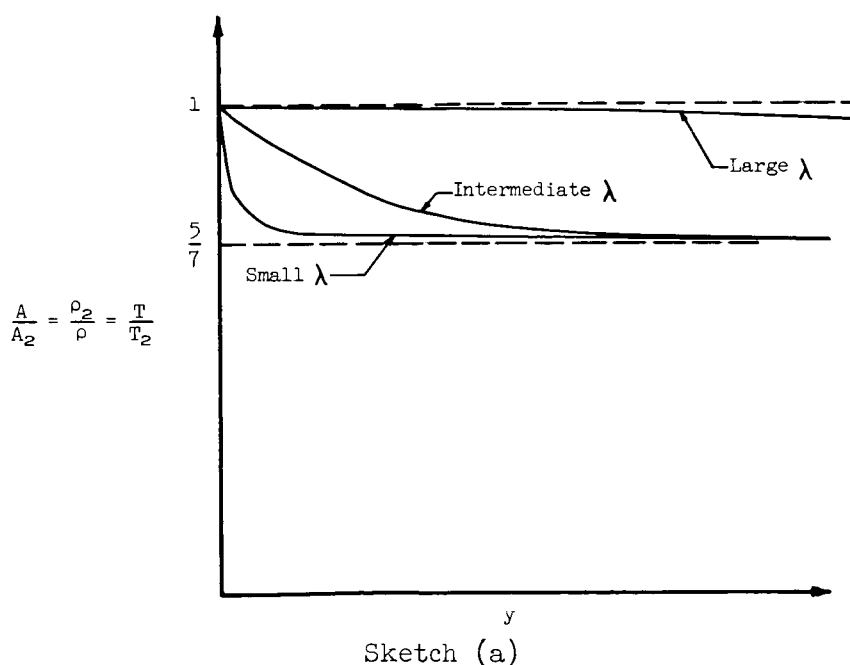
It is seen from equation (63) that the area changes by a total of 2/7 of its original size, and that this occurs over a very short distance if λ is short, and over a long distance if λ is long. For the large λ limit the flow is frozen and the cross section constant as the sketch indicates. The small λ limit is equilibrium flow, and constant cross-sectional area, constant temperature, and density. Were one to sketch A/A_2 as a function of y/λ, the three curves would coincide, indicating that λ is an appropriate unit of length, from the point of view of similarity.

<div align="center">

Simultaneous Chemical and Vibrational Relaxation
Behind a Normal Shock

</div>

The flow behind a normal shock wave where vibrational lag and dissociation of the gas are occurring simultaneously is next discussed. Freeman (ref. 6) has discussed the case without vibrational relaxation. We shall consider the case of constant cross-sectional area, so that the results apply to the interpretation of shock-tube experiments.

In a typical shock-tube experiment one might measure the pressure and the temperature as a function of position behind the shock front. One would like to deduce from this the degree of dissociation, x, as a function of position, y, and also the development of vibrational energy, e_v, as a function of position, in order to obtain the rate of the reaction and the rate of vibrational excitation. Given the state of the gas on the cold side of the shock (region 1 in sketch (b)), one can obtain the state immediately behind the shock (region 2) from an ideal gas calculation, and one can also easily obtain the state of the gas after it has reached equilibrium (region 3) from an equilibrium calculation (ref. 22). We are concerned with the flow as it proceeds from region 2 to region 3.

Sketch (b)

For this (constant area) flow the continuity equation becomes

$$\rho' u = m \tag{64}$$

and equation (6) becomes

$$\frac{dp}{du} = -1 \; ; \quad u\,\frac{du}{dh} = -1 \tag{65}$$

where the dimensionless pressure parameter $p=(p'/m)(M_{A_2}/N_0 D)$. The equation of state becomes

$$\frac{p}{\rho'} = \left(\frac{1+x}{m}\right)T \tag{66}$$

The relation between pressure and density is seen from equations (65) and (64) to be not of the polytrope form, but

$$p-p_2=\left(\frac{m}{\rho_2'} - \frac{m}{\rho'}\right) \tag{67}$$

To obtain x as a function of pressure and temperature, we only need to eliminate the density from equation (66) with the help of equations (65) and (64) to give

$$(1+x) = \frac{p}{T}(u_2+p_2-p) \tag{68}$$

Use of expression (4) for the enthalpy gives for the vibrational energy,

$$e_V=\left(h_2 + \frac{1}{2}u_2^2\right)-\left(\frac{1+x}{2}\right)^2 \frac{T^2}{p^2} - \frac{T}{2}(7+3x)-x \tag{69}$$

where expression (68) for x may be inserted into equation (69) if desired. Equations (68) and (69) yield the dissociation energy and vibrational energy of the gas as a function of position, if the pressure and temperature have been measured as a function of position. It can be seen that both the vibrations and the dissociations can be obtained from the temperature and pressure measurements.

In solving flow problems one may have the inverse situation from the experimental one just described. One may have a good idea of the relaxation times of the vibrations and the reaction, that is, one knows $x(y)$ and $e_V(y)$, but would like to calculate the effect of these rate processes on velocity, pressure, density, and temperature. Thus, x and e_V are regarded as the independent variables and the velocity, etc., is is expressed in terms of x and e_V. Again, everything is known in the

40

regions 2 and 3 and the intermediate region is of concern. The speed u is computed in terms of x and e_v, because from equations (64), (65), and (66) one immediately has density, pressure, and temperature from the knowledge of u(y). From equations (5) and (4), and with the help of equations (64), (65), and (66), a quadratic equation for velocity u is obtained:

$$\frac{u^2}{2} = \left(\frac{u_2^2}{2} + h_2\right) - h \tag{70}$$

$$= (u_2^2 + h_2) - e_v - x - \left[\frac{7+3x}{2(1+x)}\right] u(u_2 - u + p_2) \tag{71}$$

The appropriate solution is given by

$$\frac{u(x,e_v)}{u_2} = \frac{\rho_2}{\rho(x,e_v)} = \frac{\beta - \sqrt{\beta^2 - 2\alpha\delta}}{\alpha u_2} \tag{72}$$

with

$$\beta = (u_2 + p_2)\frac{7+3x}{2(1+x)}$$

$$\alpha = \frac{2(3+x)}{1+x}$$

$$\delta = \left(\frac{u_2^2}{2} + h_2\right) - (e_v + x)$$

The discarded solution of equation (71), when it is a positive real number, implies supersonic flow in region 2, a condition that cannot be realized physically.

To show, at least qualitatively, how the dissociating-vibrating gas relaxes to equilibrium, we shall use the simplest possible expressions for $e_v(y)$ and x(y) which take into account the gross features of the mutual interaction between the two processes. A quantitatively reliable treatment is not yet possible at the present state of knowledge for the coupled relaxation process of any specific diatomic gas.

A very naive approach would be to assume an exponential increase of vibrational energy, $e_V/e_{V_3} = 1 - e^{y/\lambda}$, along the shock tube and also a similar expression for x, completely ignoring any coupling between them. This assumption could lead to absurd results for, in the case that the chemical relaxation length λ_c is much shorter than the vibrational length λ_V, and the gas is fully dissociated at equilibrium, the equations would predict considerable vibrational energy in the region $\lambda_c \ll y \ll \lambda_V$, although, in fact, there are no diatomic molecules in that region and the vibrational energy should be zero.

To obtain a more reasonable expression for the relaxation process, we note from equation (23) that

$$\frac{e_V}{e_{V_3}} = \frac{1-x}{1-x_3} \frac{\epsilon(T_V)}{\epsilon(T_3)} \tag{73}$$

and we then postulate an exponential dependence for the vibrational energy per molecule rather than for the total vibrational energy (this is in agreement with Bethe-Teller theory, ref. 22):

$$\frac{e_V}{e_{V_3}} = \frac{1-x}{1-x_3} (1 - e^{-y/\lambda_V}) \tag{74}$$

We further expect physically that the degree of dissociation, x, will depend on the vibrational temperature because (if such a temperature exists) the relative probability of the diatomic state is proportional to the vibrational partition function $f_V(T_V)$. Thus $(x^2/1-x) \sim [1/f_V(T_V)]$ and then, at least for small x, $x \sim \left[1/\sqrt{f_V(T_V)} \right]$. For x near unity the the vibrational energy becomes so small anyway that the coupling must be quite unimportant. This leads us to postulate a form

$$\frac{x}{x_3} = (1 - e^{-y/\lambda_c}) \sqrt{\frac{f_V(T_3)}{f_V(T_V)}} = \frac{1 - \exp(-y/\lambda_c)}{\sqrt{1 - \exp(-y/\lambda_V - \theta/T_3)}} \tag{75}$$

It can be seen from equation (75) that even when $y/\lambda_c \gg 1$ the dissociation keeps changing as long as vibrations have not reached their equilibrium. This is physically correct because the temperature keeps

changing and the local equilibrium value of x changes along with it. One feature of these equations is that if $\lambda_V \ll \lambda_c$ or $\lambda_c \ll \lambda_V$, the rapidly relaxing variable will overshoot its equilibrium value and then return to equilibrium feeding some of its energy into the other variable. The graphs, figure 6, illustrate this point. The graphs also illustrate that the amount of dissociation at $y=\lambda_c$ is not a fixed quantity but depends on how rapidly the vibrations are reaching equilibrium, conversely, for the vibrations at $y=\lambda_V$. The graphs were drawn for a pure oxygen gas, a shock strength $M_1=10$, and a density of one-tenth of sea-level density of air. The final values of x and e_V are $x_3=0.107$, and $e_{V_3}=0.0502$. Thus, the gas is 10 percent dissociated and the approximation that $x \ll 1$, which is implicit in equation (75), is valid. Substituting equations (75) and (74) into (73) and then substituting equations (75) and (73) into (72) gives the flow velocity and the density. The latter is shown graphically for a few different values of λ_c/λ_V (fig. 7). It is evident from the figure that the dissociation process dominates the effect on density; energetically, it is more important than vibrations in this example. Further, it would not be correct for this example to divide the relaxation region into two parts in each of which only one variable relaxes - no matter what the ratio of λ_c/λ_V. The only case where the density is not a smoothly varying monotonic function is the case where $\lambda_c=0$. There an overshoot in density appears followed by a drop below equilibrium and finally reaches equilibrium from below. The various curves of $\rho(y)/\rho(0)$ in figure 7 form a sequence varying continuously and smoothly with the parameter λ_c/λ_V.

CONCLUDING REMARKS

If appropriate units are used (ref. 5), the equations for the thermodynamics and one-dimensional flow of a dissociating and vibrating gas in equilibrium are not prohibitively complicated. They can all be expressed in algebraic form when electronic excitations are neglected, but without resorting to Lighthill's ideal gas. The resulting formulas for equilibrium flow are accurate to within a few percent at temperatures where ionization is negligible. It is found that for flow of the gas in chemical equilibrium, the temperature and the degree of dissociation are convenient independent variables to use. They are related through the entropy, a constant along the flow. With rather slight modifications the formulas worked out here can be applied to a gas mixture such as air.

There also exist isentropic flows in which the vibrations are in equilibrium and the reaction is frozen, and also flows in which the reaction is in equilibrium but the vibrations are frozen. The distinction is made between constant vibrational energy and constant vibrational temperature flow. The latter is expected to correspond to the observable frozen vibrations flow.

The nonequilibrium flow analysis is much simplified by the introduction of a vibrational temperature. The entropy becomes a point function of the four variables, temperature, density, degree of dissociation, and vibrational energy.

Flow relaxing with a finite time is qualitatively different from frozen or equilibrium flow because the entropy increases along the streamtube. The flow cannot be treated with the same generality as isentropic flow because some specific mathematical constraint is required to fully specify the flow. Below are given some of the detailed results which come from the examples treated:

1. In the relaxation region behind a shock wave in a shock tube, pressure and density are related by a simple formula which is not of the polytrope form.

2. If the relaxing flow behind a normal shock is at constant density, or at constant pressure, the streamtube contracts. The contraction for constant density flow is larger, the higher the free-stream Mach number. For constant pressure the total area change is about a factor of 2/7.

3. Relaxing isothermal flow behind a normal shock corresponds to a rapidly expanding streamtube.

4. If in a shock tube both vibrational relaxation and chemical relaxation are occurring behind the normal shock wave, the degree of dissociation and the degree of vibrational excitation can be calculated from measurements of the pressure and temperature distributions behind the wave.

When vibration and dissociation are both occurring simultaneously, the two processes can, in general, be expected to interact. The coupling can be included in a simple model of the relaxation. When the reaction is relatively very fast, this model of the relaxation process yields the result that the density overshoots its equilibrium value, decreases to below its equilibrium value, and finally reaches equilibrium from below.

Ames Research Center
    National Aeronautics and Space Administration
        Moffett Field, Calif., Feb. 26, 1959

APPENDIX A

DERIVATION OF ENTROPY EQUATION

The idea of evaluating the entropy of a gas with vibrational temperature T_V and with translations and rotations at a temperature T is to calculate the entropy of the two systems separately and then to add them. The entropy of the system of harmonic oscillators alone at temperature T_V (see any textbook on statistical mechanics) is

$$S_V = (1-x)\left[\frac{\theta/T_V}{e^{\theta/T_V}-1} - \log(1-e^{-\theta/T_V})\right] \tag{A1}$$

The entropy of the mixture of free atoms and dumbbell diatomic molecules at a temperature T is:

$$S_{tr+rot} = \frac{x+5}{2}\log T - 2x\log 2\rho x - (1-x)\log(1-x)\rho + xS^+ \tag{A2}$$

where S^+ is a constant. The corresponding energies are

$$e_V = \frac{(1-x)\theta}{e^{\theta/T_V}-1}, \qquad e_{tr+rot} = \frac{5+x}{2}T \tag{A3}$$

From equation (A3) we see that equation (A1) may be written

$$S_V = \frac{e_V}{T_V} - (1-x)\log(1-e^{-\theta/T_V})$$

$$dS_V = \frac{de_V}{T_V} + \log(1-e^{-\theta/T_V})dx \tag{A4}$$

Differentiating equation (A2) gives:

$$dS_{tr+rot} = \frac{x+5}{2} \frac{dT}{T} - (1+x) \frac{d\rho}{\rho} + \left[\log \frac{(1-x)\sqrt{T}}{4\rho'x^2} - 1 + S^+ \right] dx \qquad (A5)$$

The addition of equations (A4) and (A5) yields

$$dS = dS_v + dS_{tr+rot}$$

$$dS = \frac{de_v}{T_v} + \frac{x+5}{2} \frac{dT}{T} - (1+x) \frac{d\rho}{\rho} + \left[\log \frac{(1-x)\sqrt{T}\,(1-e^{-\theta/T_v})}{\rho'x^2} + const \right] dx$$

$$(A6)$$

The const can be evaluated from the entropy constant S^+. Alternatively it may be evaluated from the equilibrium constant as follows:

At equilibrium comparison of equation (A6) with equation (10) gives

$$const + \log \frac{(1-x)\sqrt{T}\,(1-e^{-\theta/T})}{\rho'x^2} = \frac{1}{T} + \frac{1}{2} \qquad (A7)$$

Furthermore, the equation for the equilibrium constant is (again, see any book on statistical mechanics):

$$\frac{\rho'x^2}{1-x} = C\sqrt{T}\,(1-e^{-\theta/T})e^{-1/T} \qquad (A8)$$

where C is a known numerical constant characteristic of the species of gas (values are tabulated in appendix B). Let us choose C as the unit of density; then comparison of equations (A7) and (A8) shows that the constant in equation (A7), and also (A6), is 1/2. This completes the derivation of equation (14).

APPENDIX B

CHARACTERISTIC CONSTANTS FOR VARIOUS GASES

Gas	M_{A_2}, gm/mol	θ_V, °K	θ_R, °K	θ_D, °K	f_A^e		$f_{A_2}^e$		C, gm/cm³
H_2	2	6324	84.971	51,950	1		1		2.130
O_2	32	2274	2.059	58,960	8.8	$\left(5+3\,e^{\frac{-228}{T'}} + e^{\frac{-327}{T'}}\right)$	3.3	$\left(3+2\,e^{\frac{-11,300}{T'}}\right)$	1317
N_2	28	3396	2.847	113,240	4		1		1237
Cl_2	71	812.9	.3477	28,730	4	$\left(4+2\,e^{\frac{-1,277}{T'}}\right)$	1		778.6
Br_2	160	465.1	.1156	22,880	4	$\left(4+2\,e^{\frac{-5,223}{T'}}\right)$	1		1761
I_2	254	308.8	.05340	17,895	4	$\left(4+2\,e^{\frac{-10,910}{T'}}\right)$	1	$\left(1+6\,e^{\frac{-17,107}{T'}}\right)$	2285

Note:

1. Symbols: $\theta_V = \dfrac{h\nu}{k}$, $\theta_R = \dfrac{h^2}{8\pi^2 I_k}$, $\theta_D = \dfrac{D}{k}$, $\dfrac{\theta_V}{\theta_D} = \theta$

    I = moment of inertia of the diatomic molecule

2. Conversion of units: The factors used were 1 e_V = 11,607° K, 1 cm⁻¹ = 1,439° K; a convenient table for converting energy units is given in reference 18, page 471.

3. The electronic partition functions f_A^e and $f_{A_2}^e$ are constants to the approximation used here. These constants represent essentially the degeneracy of the ground state of the atom or molecule. Whenever they are not constant, the exact electronic partition functions with their temperature dependence are given in parentheses. If working with temperatures at which the constant value given above is not the best numerical approximation to the electronic partition function, one should correct C accordingly. For example, if working with chlorine near 5000° K, then f_A^e = 5.5, not 4; the value of C is then corrected (see below) by multiplication by $(5.5/4)^2$, nearly a factor of 2. The constants given for oxygen give results for C that are within 5 percent in the temperature range for 1500° K to 8000° K, so that x is within 2-1/2 percent of its exact value.

4. The quantity

$$C = \frac{(\pi k)^{3/2}}{h^3 N_O^{5/2}} \theta_D^{1/2} \theta_R \frac{(f_A^{\ e})^2}{f_{A_2}^{\ e}} M_A^{5/2}$$

$$= 1.10 \times 10^{-4} \theta_D^{1/2} \theta_R \frac{(f_A^{\ e})^2}{f_{A_2}^{\ e}} M_A^{5/2} \frac{gm}{cm^3}$$

APPENDIX C

DISCUSSION OF THE EQUILIBRIUM CONSTANT

The quantity called the equilibrium constant in this report is

$$K(T) = \rho \frac{x^2}{1-x} = \text{const } \frac{n_A{}^2}{n_{A_2}}$$

It is a measure of the probability (or number) of two free atoms in the gas relative to the probability of a diatomic molecule (two bound atoms). According to statistical mechanics, these probabilities can be expressed in terms of the partition function f_A for a free atom and the partition function f_{A_2} for the diatomic molecule.

$$\frac{n_A{}^2}{n_{A_2}} = \frac{f_A{}^2}{f_{A_2}} = \text{const } \frac{(T^{3/2})^2 e^{-1/T}}{(T^{5/2})(1-e^{-\theta/T})^{-1}} = \text{const } \sqrt{T}\ (1-e^{-\theta/T})e^{-1/T}$$

In the numerator the $T^{3/2}$ comes from the three translational degrees of freedom of each atom. In the denominator the $T^{5/2}$ is from the five degrees of freedom of a dumbbell diatomic molecule – three degrees of translation and two of rotation. (The spinning about its own axis is not counted as a degree of freedom.) The factor $(1-e^{\theta/T})^{-1}$ is the part of the molecular partition function due to the vibrational degree of freedom. It is noted that vibrations are an exception to the rule: Each degree of freedom contributes a factor $T^{1/2}$. (Similarly, it is seen in the text that vibrations do not contribute just $1/2\ k$ to the specific heat, but an amount which depends on temperature.)

Finally, the $e^{-1/T}$ factor simply takes into account the fact that between the ground state of a diatomic molecule and the ground state of the dissociated atoms there is a certain dissociation energy D. If temperature were expressed in degrees instead of the dimensionless T used, the factor would be $e^{-D/kT}$.

The derivation of the equilibrium constant and calculation of the partition function can be found in the books on statistical mechanics in the bibliography.

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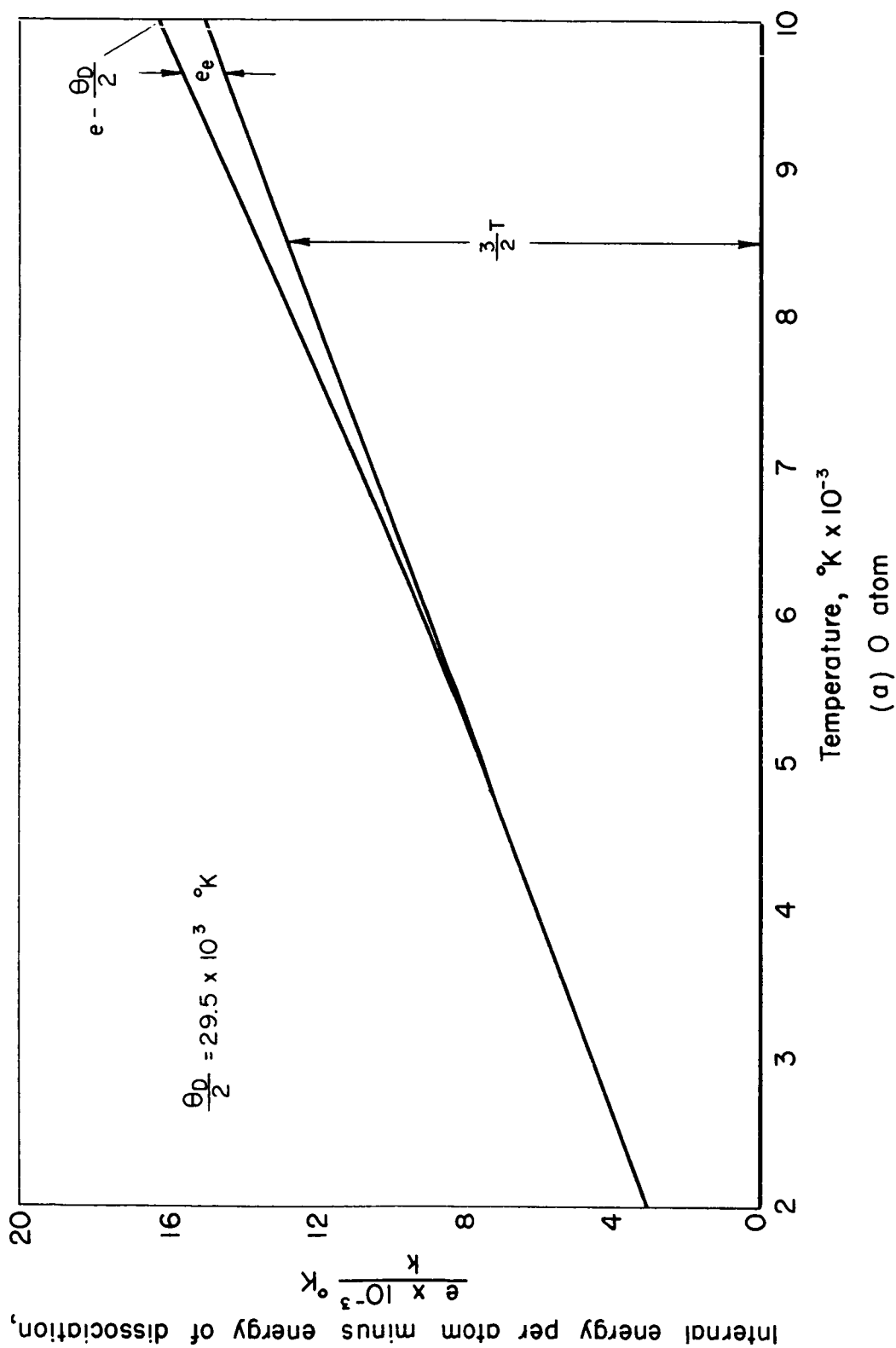
Figure 1.- Distribution of average internal energy as a function of temperature.

(b) N atom
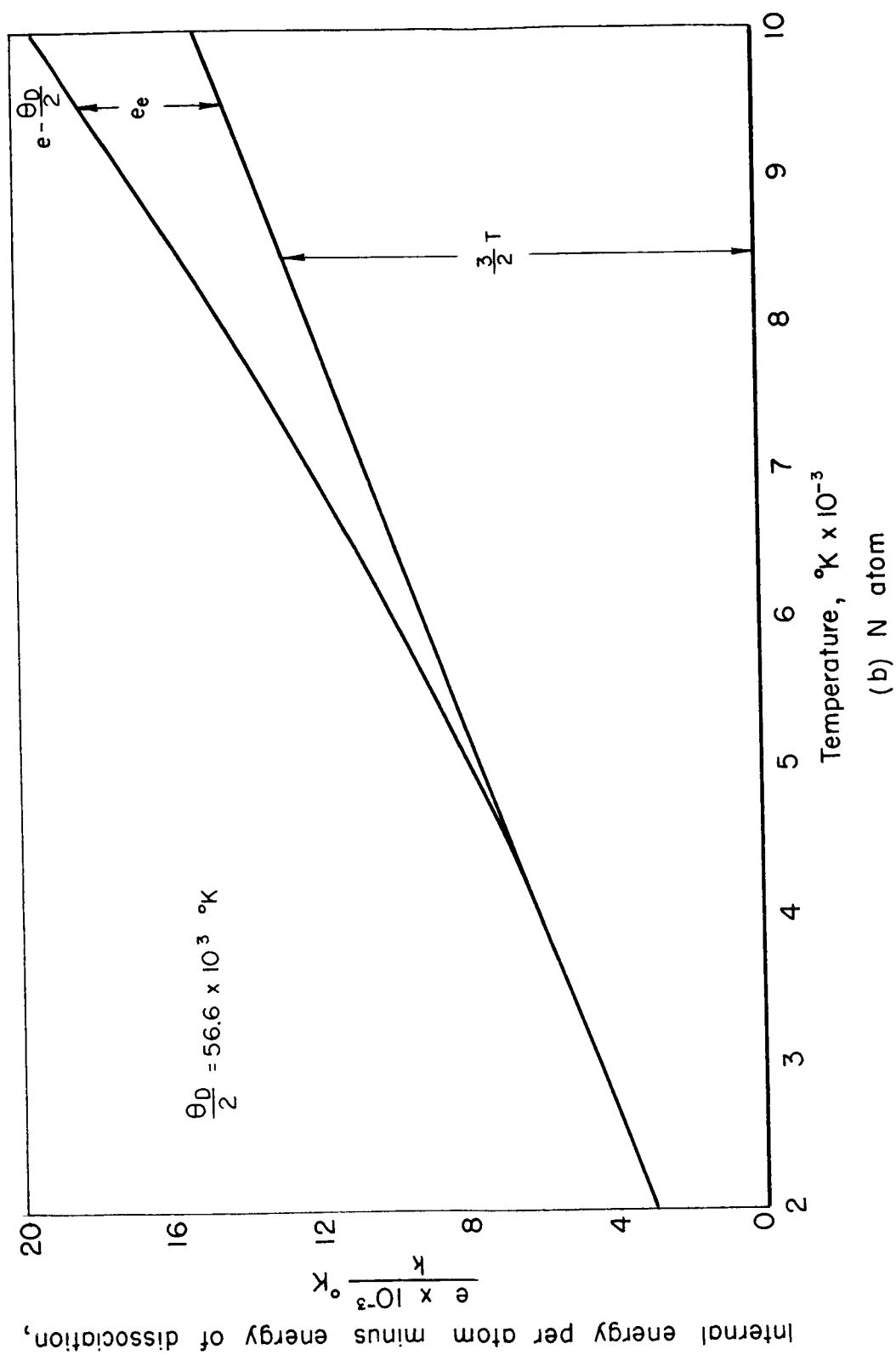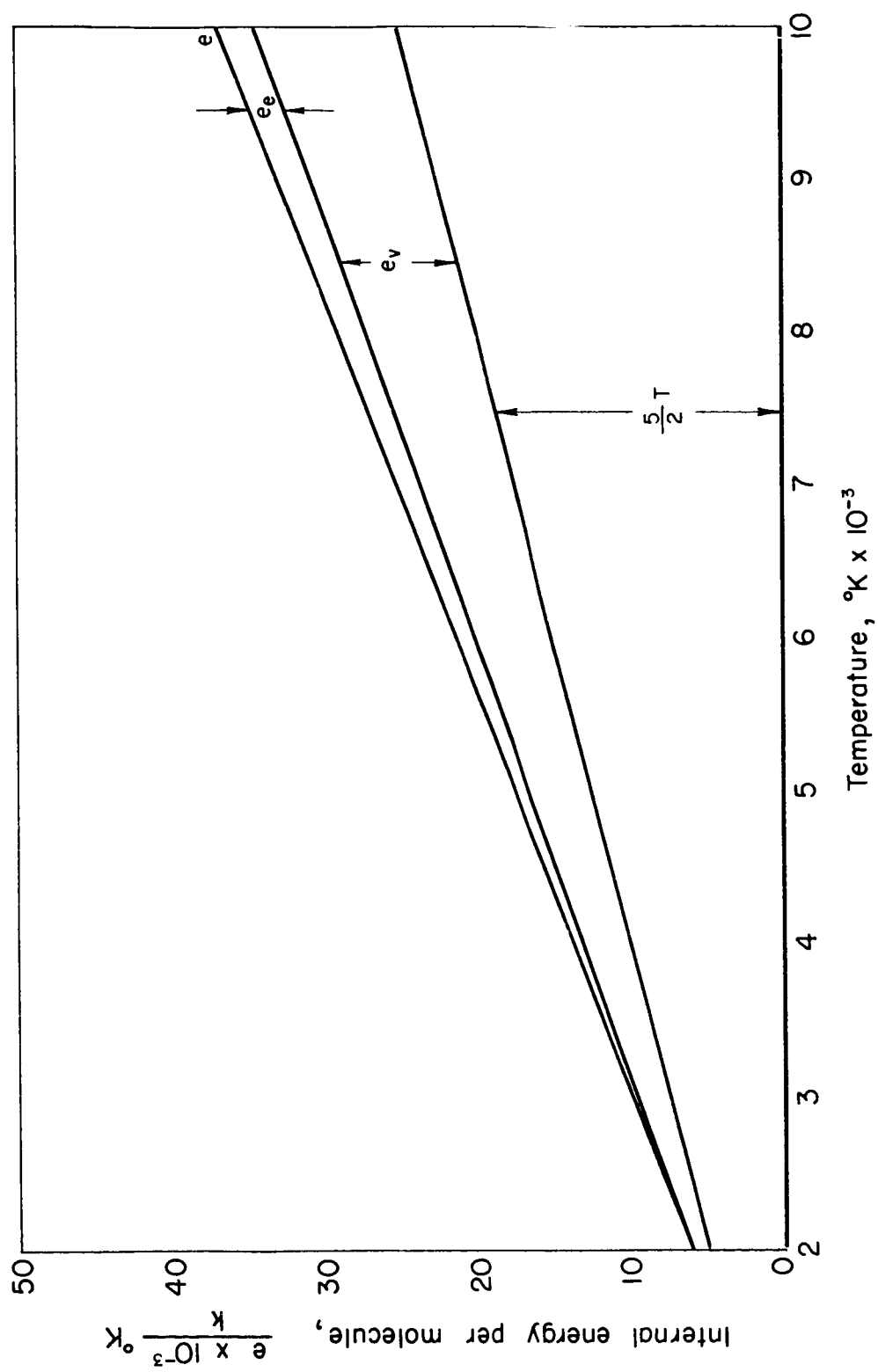
Figure 1.- Continued.

(c) O_2 molecule

Figure 1.- Continued.

(d) N_2 molecule
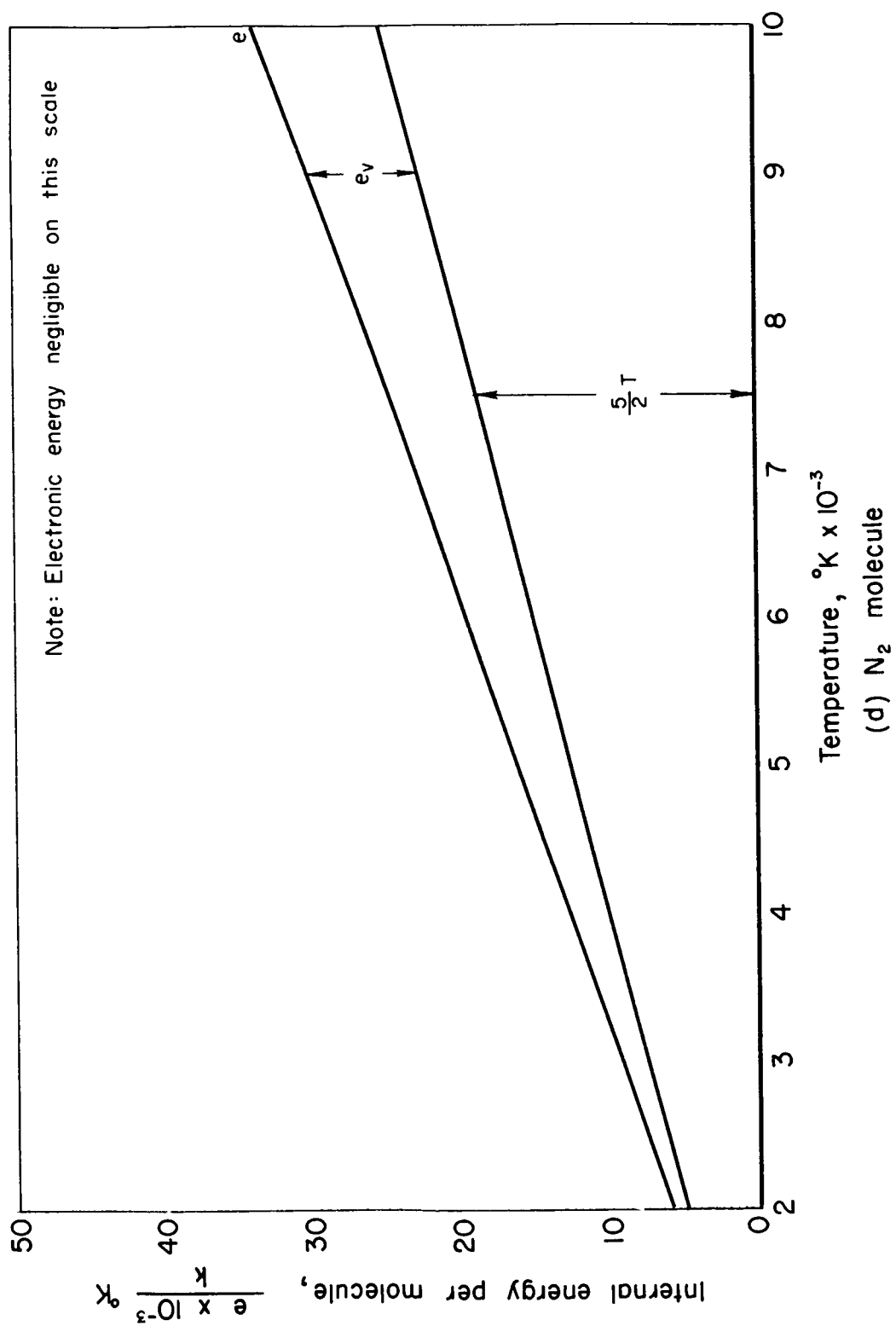
Figure 1.- Concluded.
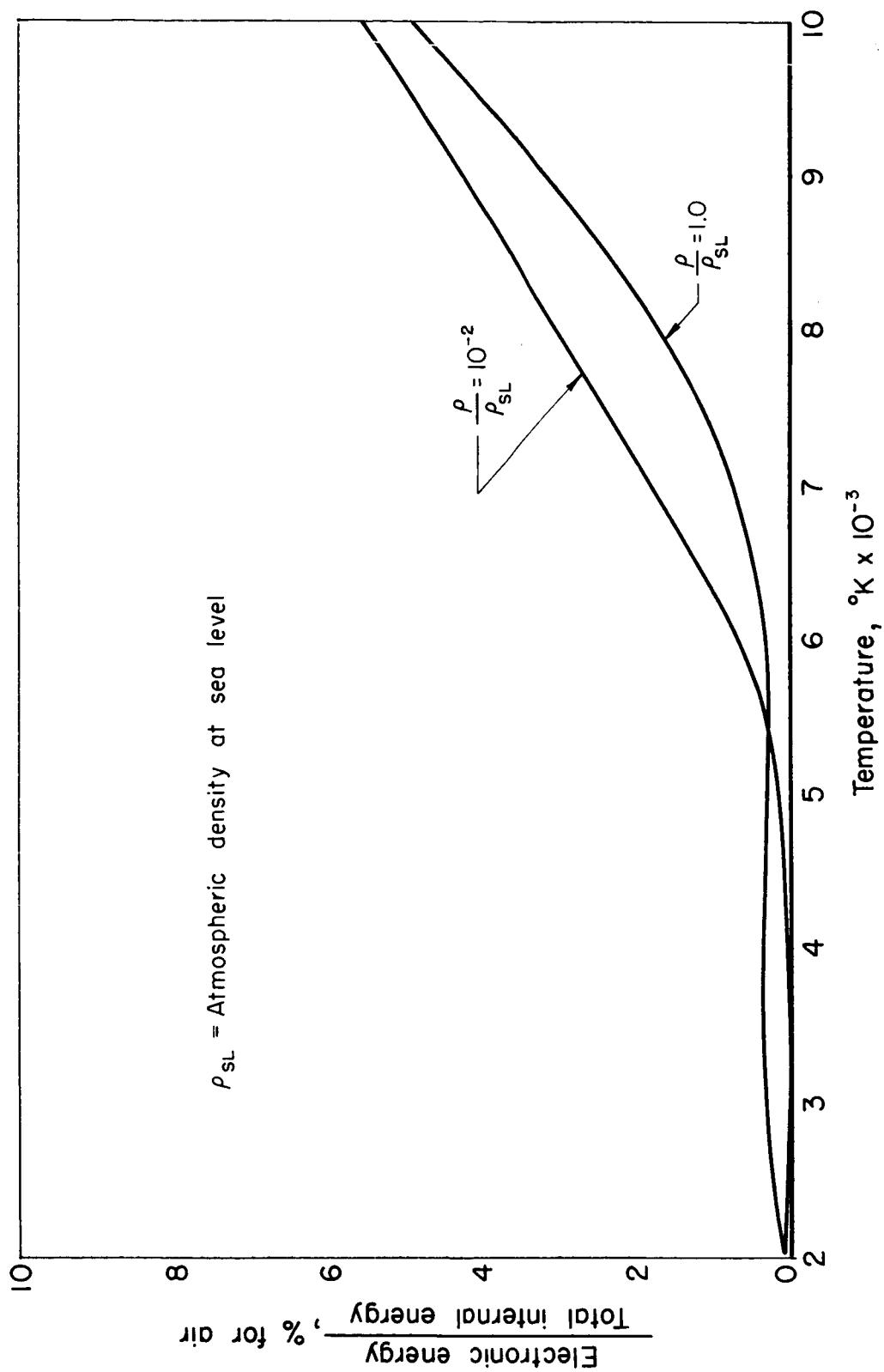
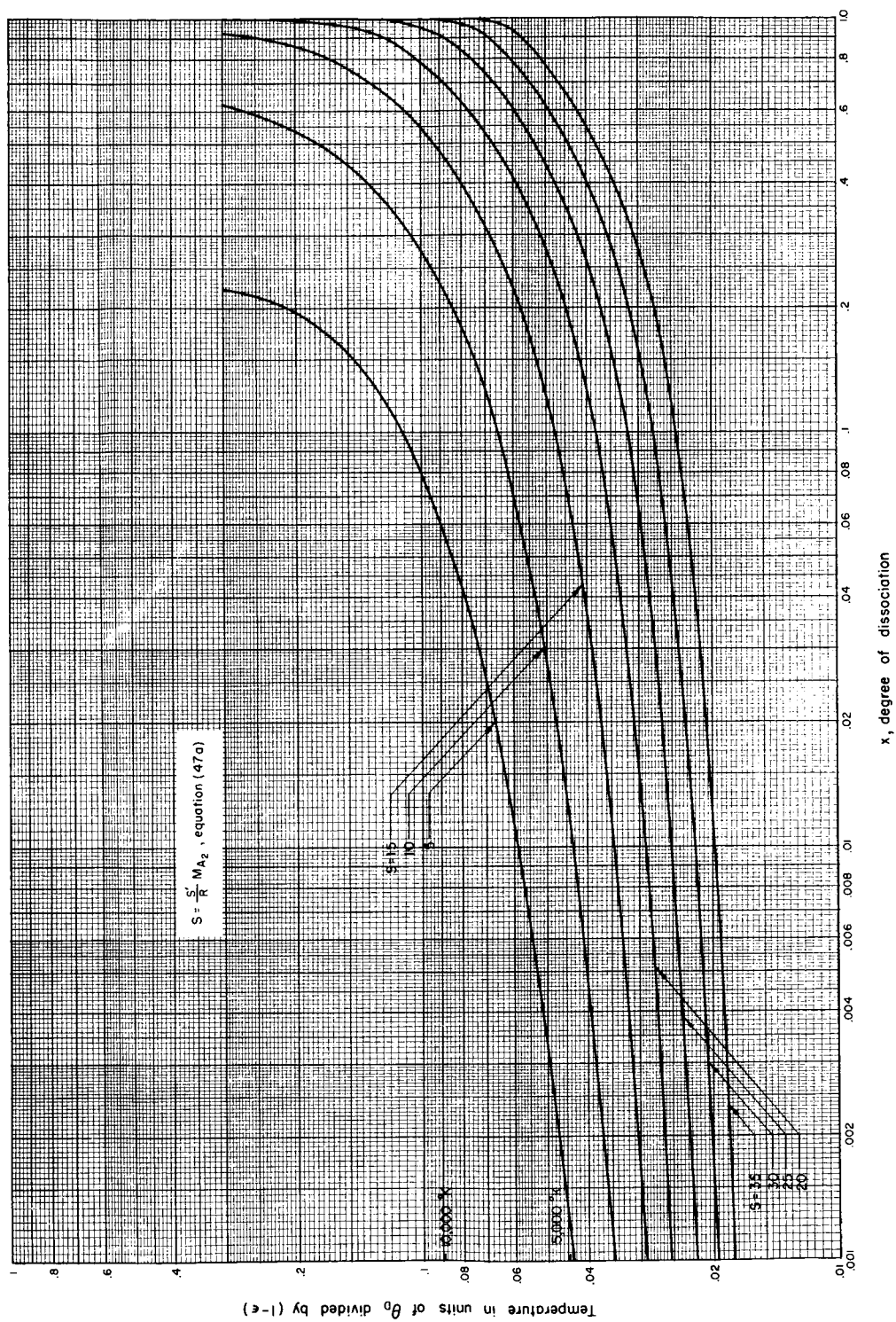Figure 2.- The percent of internal energy in the form of electronic excitations for air.

58
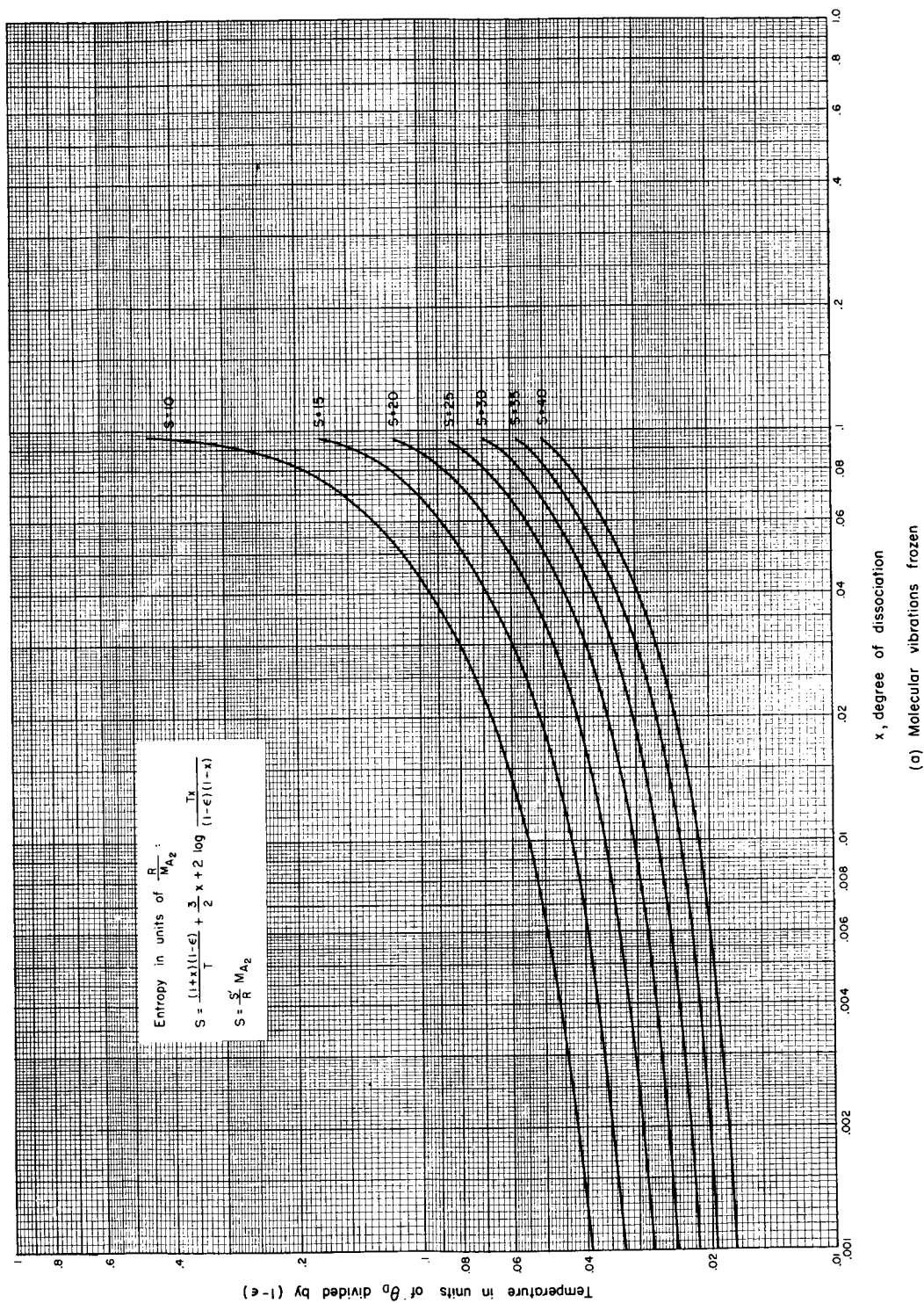
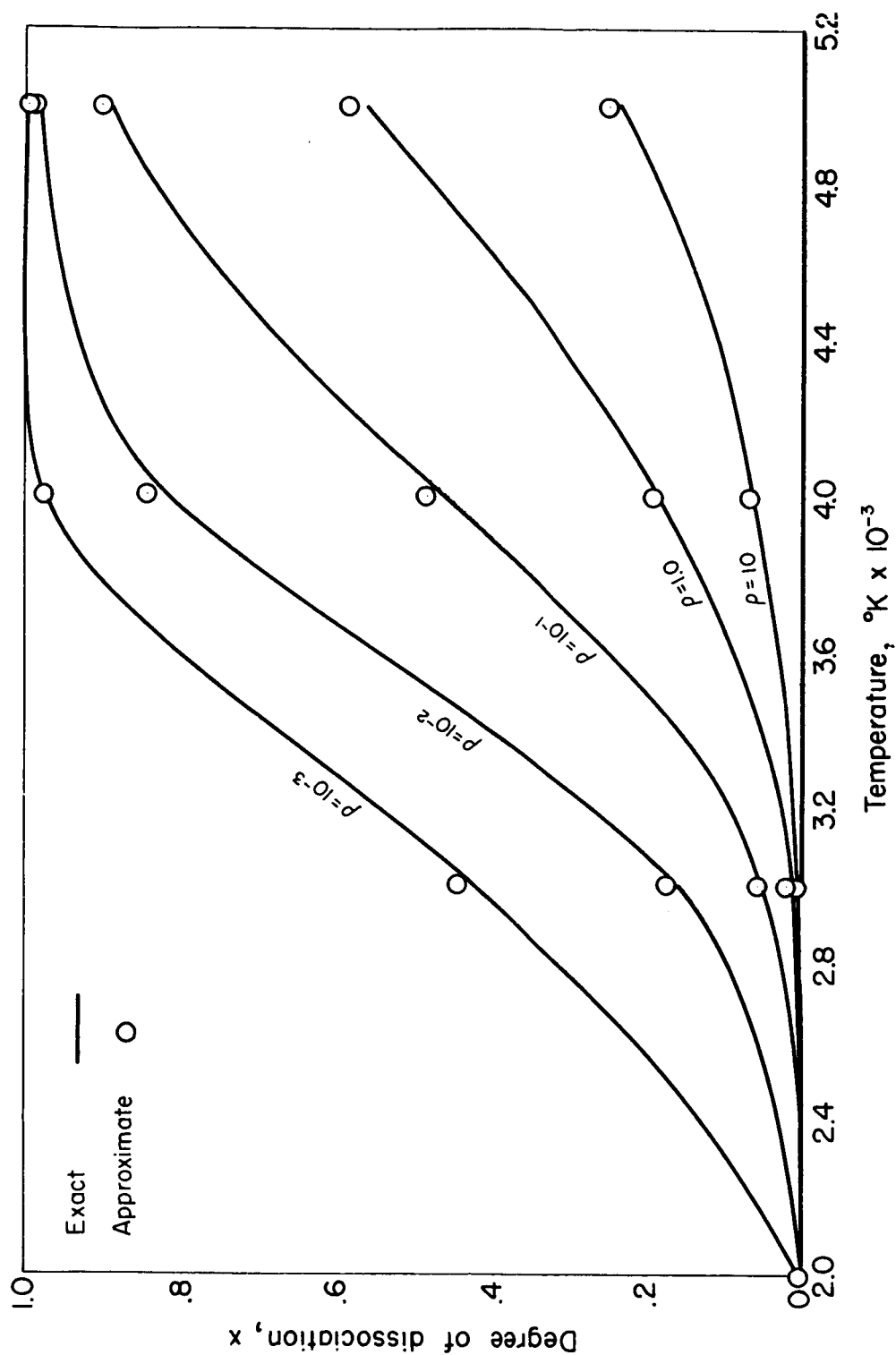Figure 3.- Isentropes for dissociating diatomic gas.

x, degree of dissociation

(a) Molecular vibrations frozen

Entropy in units of $\frac{R}{M_{A_2}}$:

$$S = \frac{(1+x)(1-\epsilon)}{T} + \frac{3}{2}x + 2\log\frac{Tx}{(1-\epsilon)(1-x)}$$

$$S = \frac{S'}{R}M_{A_2}$$

Temperature in units of θ_D divided by $(1-\epsilon)$

(b) Oxygen in full equilibrium

Figure 3.- Continued.

x, degree of dissociation

(c) Nitrogen in full equilibrium

Figure 3.- Concluded.
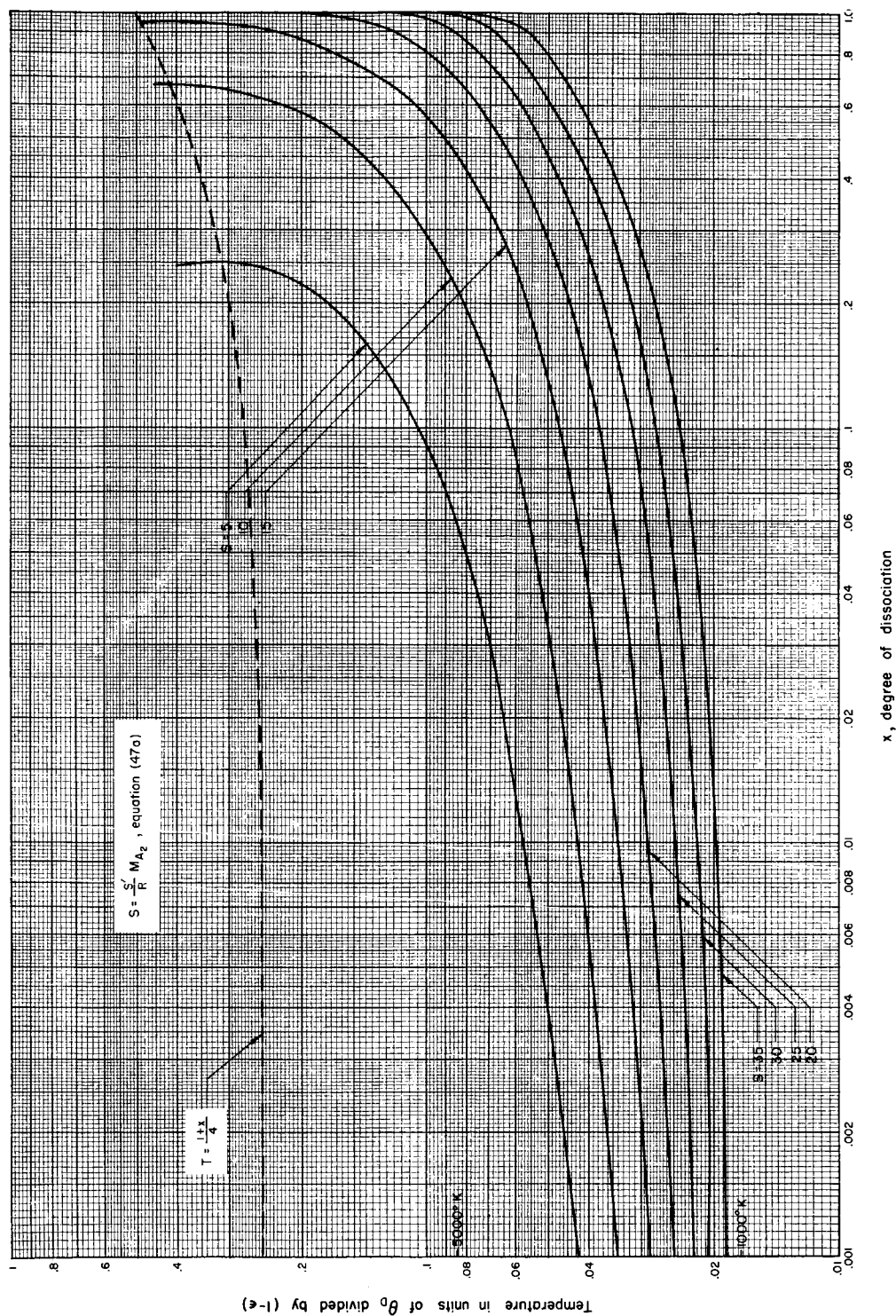
(a) Equilibrium dissociation as a function of temperature.

Figure 4.- Comparison of exact tabulated quantities for oxygen with those obtained by the mathematical model of the gas used in the present paper.
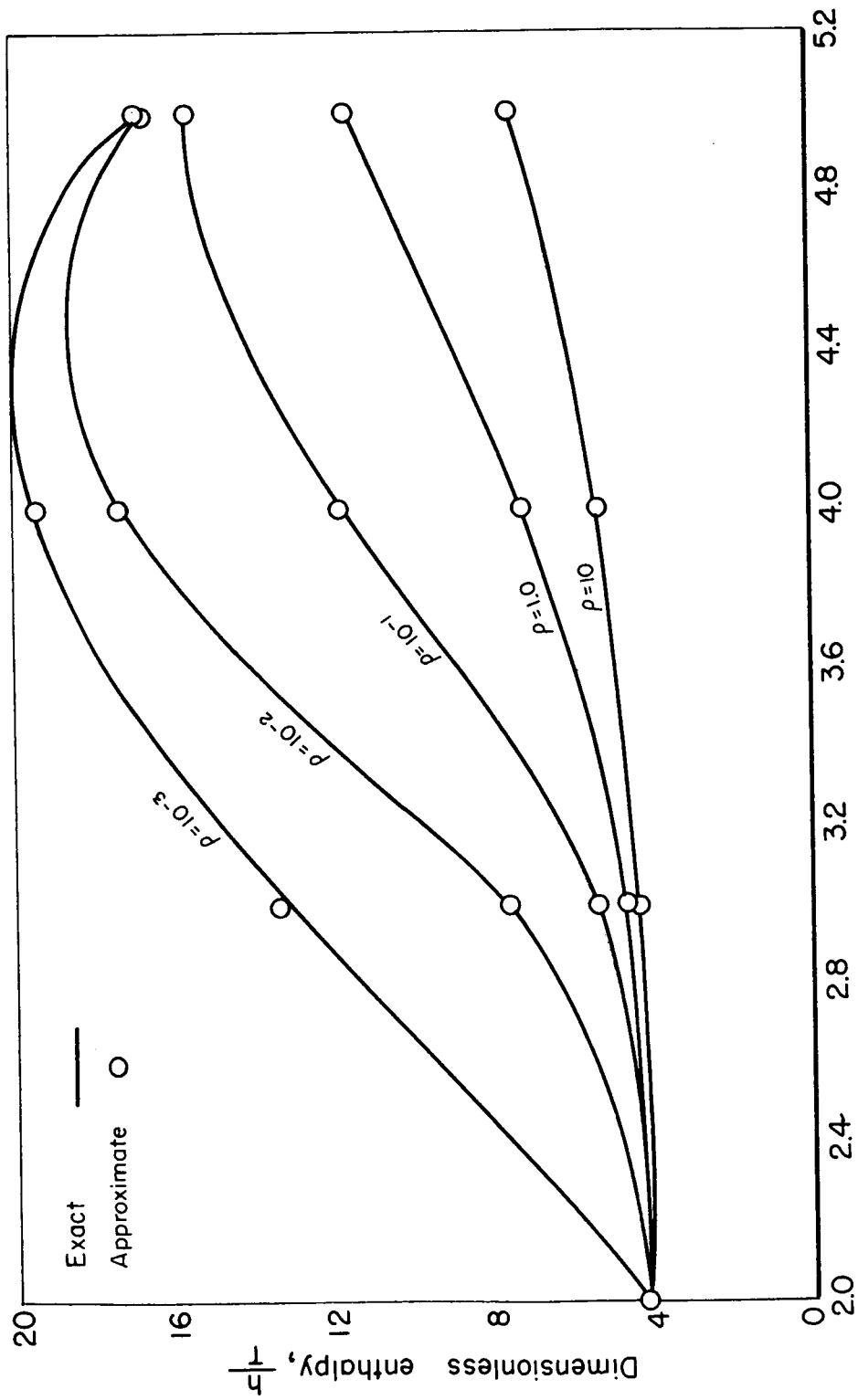
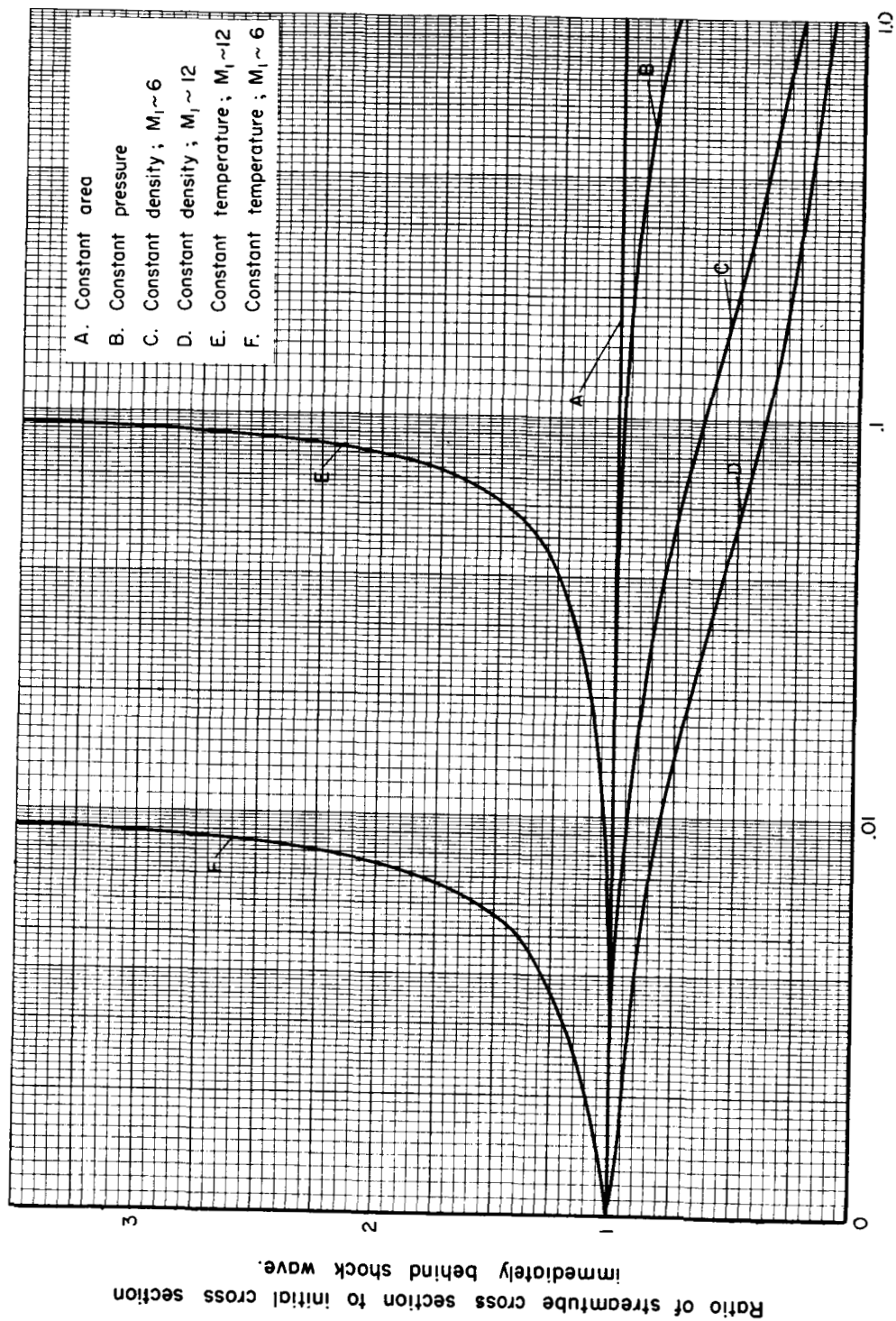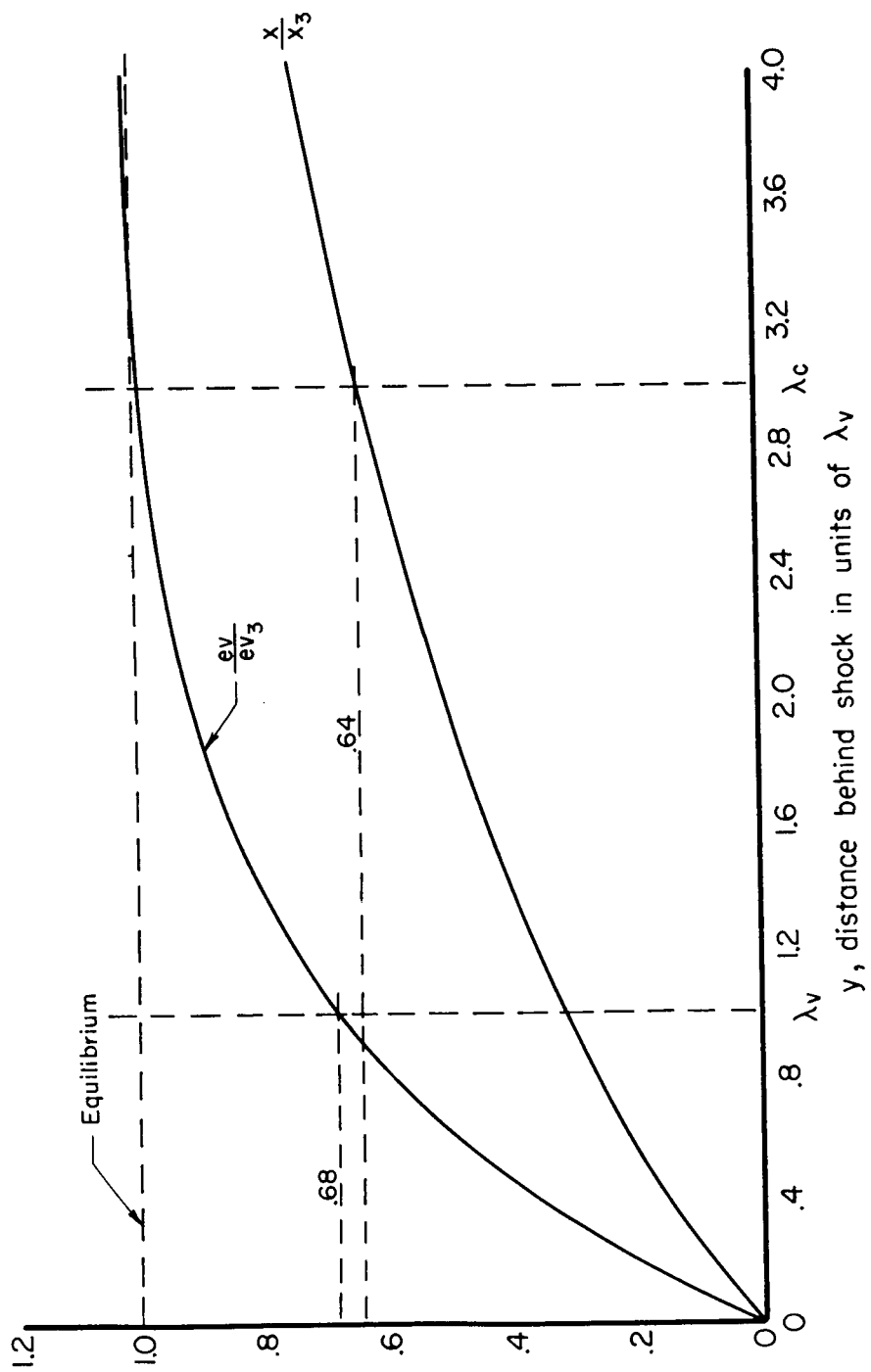(b) Equilibrium enthalpy as a function of temperature.
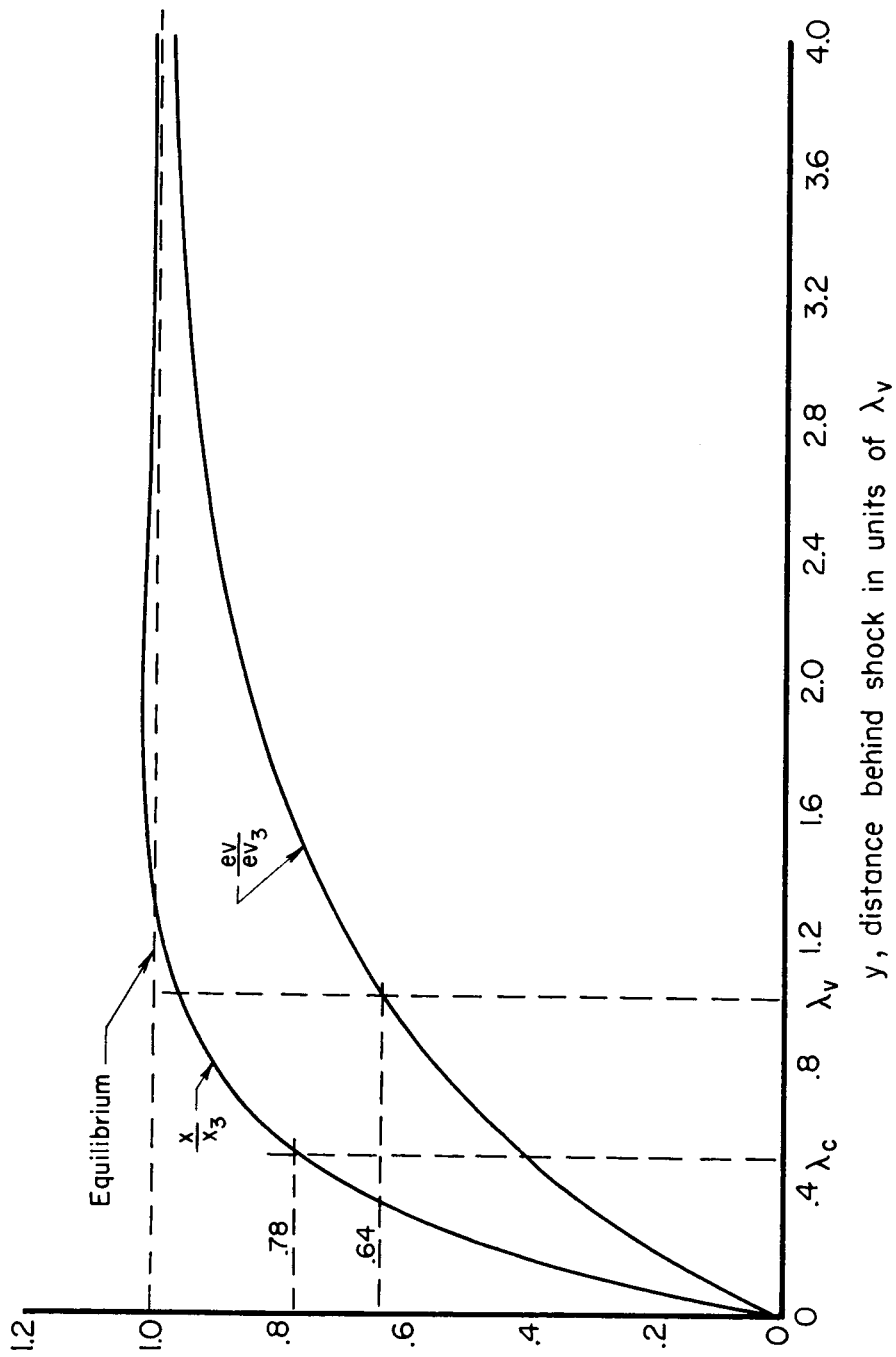
Figure 4.- Concluded.

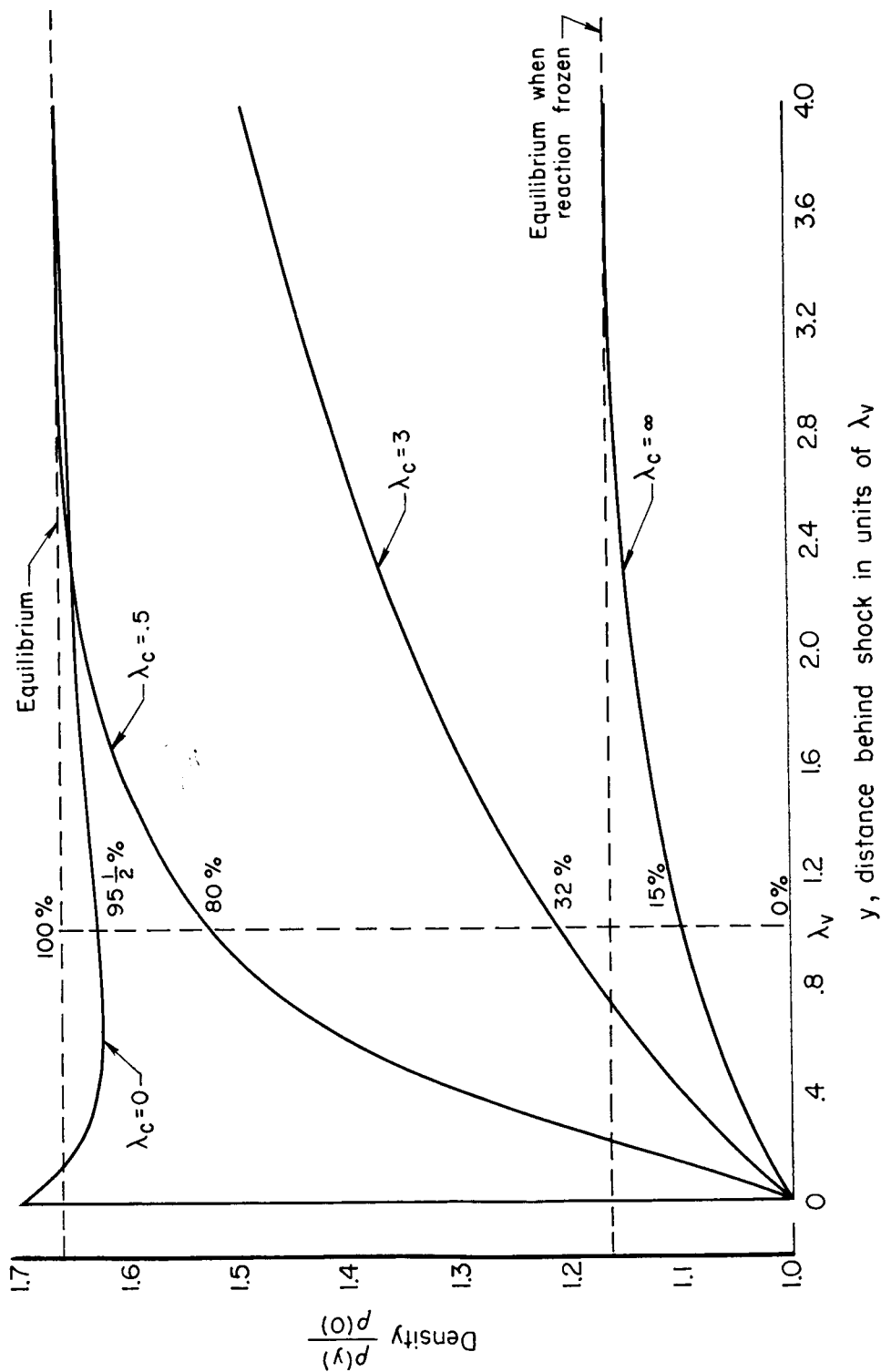Figure 5.- Effect of vibrational relaxation on shape of streamtubes behind a normal shock, for differing constraints.

Figure 6.- The simultaneous approach to equilibrium of the molecular vibrations and dissociation behind a normal shock.

(a) $\lambda_c = 3\lambda_v$

(b) $\lambda_c = .5\lambda_v$

Figure 6.- Concluded.

Figure 7.- Density variation of a gas relaxing behind a normal shock for different values of λ_c/λ_v.